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August 1980

EVALUATION OF HOT ACID TREATMENT FOR MUNICIPAL SLUDGE CONDITIONING

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Land application is an attractive method for final disposal of sludge solids. However, this method has not been fully exploited because of the potential environmental risk certain concentrations of heavy metals in sludge present. In some cases, the concentrations of heavy metals must be reduced to acceptable levels prior to land disposal. This report presents an investigation of a process designed to remove heavy metals from sludge. The process involves both acidification and heating of the sludge. Results show that the process has potential for good solubilization and removal of toxic heavy metals and, in addition, destroys essentially all pathogens and improves the dewaterability of the sludge. A preliminary economic analysis of the process indicates that it is quite cost-competitive with alternative stabilization/conditioning processes.

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Laboratory

ABSTRACT

Bench-scale tests were conducted to evaluate the technical and economic feasibility of the hot acid process for stabilization/conditioning of municipal sewage sludge. This process involves acidification of the sludge (pH 1.5-3) and heating to temperatures below boiling (∿95°C). Test results indicate that the process improves the dewaterability of the sludge, destroys essentially all pathogens, and preferentially solubilizes certain heavy metals relative to nitrogen and organics. The process demonstrated the potential for good solubilization and removal of toxic heavy metals including cadmium, zinc, and nickel with minimal solubilization of nitrogen. Thus the hot acid process improves the desirability of sludge solids for land application. A preliminary economic analysis of the process indicates that it is quite cost-competitive with alternative stabilization/conditioning processes.

This report was submitted in fulfillment of Contract No. 68-03-2459 by the Walden Division of Abcor, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period of September 26, 1976 to February 11, 1979 and work was completed as of April 6, 1979.

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SECTION 1

INTRODUCTION

The disposal of sludge from municipal wastewater treatment plants is a problem of increasing complexity and magnitude. The amount of sewage sludge produced in the United States is expected to increase over the next several years because of increases in the sewered population and the upgrading of existing wastewater treatment plants. Simultaneously, environmental restrictions are decreasing the options available for sludge disposal. At present, four techniques for sludge disposal are in general use (1):

- -- sanitary landfill,
- -- ocean disposal,
- -- incineration with landfill of ash and scrubber sludge, and
- -- land application.

Of these, ocean disposal is being phased out by 1981.

Of the various options listed above, land application is the only option that utilizes sludge in a beneficial manner. When applied to land, sludge provides an excellent soil conditioner and results in the conservation and reuse of organic matter, nitrogen, phosphorus, and certain trace elements, all of which are necessary plant nutrients. At present, only about 25% of the sludge produced is applied to land(2), and only part of that is applied to cropland. On a national basis there is more than enough cropland available to accomodate all of the sludge produced; however in the Northeast the percentage of the cropland required for land application of sludge is higher than the national average. (In New Jersey, for example, it is projected that 55% of the cropland would be required for land application of sludge by 1985(2)). Thus, while the availability of land could be a limiting factor in certain localized areas, the application of sludge to land appears to be the most promising technique presently available for utilization/disposal of sludge.

The land application of sludge, however, does have some potential limitations particularly where the land is to be used for food-chain crops. Of particular concern is the uptake of heavy metals such as cadmium, zinc, nickel, copper, and molybdenum which can accumulate in plants and may pose a hazard to plants, animals, or humans (2). Of these potentially hazardous metals, cadmium is the metal of greatest environmental concern. The daily dietary intake of cadmium for U.S. adults approximates the total tolerable daily intake proposed by the Food and Agriculture Organization and the World

Health Organization(3). Because of the potential of certain food-chain crops to accumulate significantly increased cadmium levels from sewage sludge applied to land, rules have been proposed(4) for limiting and monitoring the land application of cadmium bearing sludges to food-chain crops.

In addition to heavy metals, the presence of pathogens and pesticides (and other persistant organics) in the sludge are also of concern(4). Pathogens may create a public health hazard, and pesticides and heavy metals could be ingested directly if the sludge is applied in such a way as to adhere to the edible portion of the crops. While lead is not a potentially hazardous metal with respect to plant uptake, the direct ingestion of lead (in addition to cadmium) should be avoided because of the proximity of the current daily intake to the proposed tolerable level(3).

While there are many municipal sludges that, when stabilized, are suitable for direct application to land, many others contain high concentrations of cadmium or other heavy metals. None of the sludge stabilization processes in current use (e.g. anaerobic digestion, aerobic digestion, thermal treatment (190°C), lime treatment, pasturization (70°C), etc.) is capable of removing significant quantities of heavy metals. Thermal treatment, for example, has been shown to remove approximately 72% of the nitrogen content from sludge solids but it does not remove significant quantities of heavy metals (5,6,7). Thus thermal treatment is detrimental to the soil conditioning value of the sludge solids.

The objective of this program was to evaluate and develop a new process for the treatment of municipal wastewater sludge. This process was invented by Champion International Corporation (patent applied for), and Abcor, Inc. has an option to negotiate an exclusive liscense for its commercialization. In brief, the process consists of acidifying the sludge (pH approximately 1.5 to 3) and heating it to a temperature below boiling (80 to 100°C) for a relatively short time (10 to 60 minutes). This "hot acid treatment" process:

1. improves the dewaterability of the sludge,
2. destroys essentially all pathogens, and
3. preferrentially solubilizes heavy metals relative to nitrogen and organics.

The preferred application for this new process is for stabilization/conditioning of thickened waste activated sludge (WAS) or mixtures of primary sludge and thickened WAS. Following hot acid digestion, the solids would be separated from the liquor using appropriate dewatering equipment. Neutralization of solids (possibly by impregnation with anhydrous ammonia to simultaneously increase nitrogen levels) may be required prior to land application. The liquor from the hot acid digestion would be treated with lime to precipitate the solubilized heavy metals before recycling the liquor to secondary treatment. The heavy metal sludge would be dewatered and disposed of in a secured landfill or by other appropriate techniques.

Ideally, the hot acid process would be similar in concept and application to the thermal conditioning process. Both would stabilize the sludge and condition it for dewatering in a single operation. However, the unique advantage of the hot acid process would be its ability to solubilize heavy metals to a much greater degree than organics and nitrogen. This process, if successfully developed to commercialization, could provide economical sludge stabilization while upgrading the quality of solids for disposal by land application, and could make land application a viable utilization/disposal option for many municipalities where high levels of heavy metals currently necessitate disposal by other alternatives.

SECTION 2

CONCLUSIONS

Bench-scale tests were conducted to evaluate the effects of the primary process variables, pH, temperature, and time, on the performance characteristics of the hot acid process. These variables were investigated over the ranges of: pH 2 to 3, temperature 80 to 95°C, and digestion time 10 to 60 minutes. Four sludges, two waste activated sludges and two primary-WAS mixtures, were evaluated during these tests. The following conclusions are based on the results of these tests.

1. Within the ranges investigated, the pH had the most significant influence on the rate of solid-liquid separation following hot acid treatment. For all sludges the optimum pH for solids separation was 2.5. The preferred temperature level was 95°C, but digestion time, within the range investigated, did not have a pronounced influence on the solids separation rate.
2. The amount of concentrated sulfuric acid required to reduce the pH of the sludge to 2.5 was 70-100 kg/dmt (dry metric ton). At an acid usage of 100 kg/dmt the cost for acid would be $4.95/dmt ($4.50/dst (dry short ton)) of sludge solids. The acid costs for the process are therefore quite reasonable and operation at even lower pH's cannot be ruled out on the basis of acid cost.
3. The primary process variables did not appear to have a significant influence on the solubilization of suspended solids. Over the range of variables investigated the average solubilization of suspended solids ranged from 6.2% to 10.6% for the four sludges tested.
4. The pH and temperature had a significant effect on the degree of organics solubilization, as determined by COD. Lower pH and higher temperature promoted greater COD solubilization. Within the range of variables investigated the degree of COD solubilization was generally <10%.
5. The pH was the only variable which had a significant influence on zinc solubilization. Lower pH's resulted in greater solubilization. Solubilizations as high as 80% were determined for zinc during these tests. On the other hand, solubilizations of copper at the conditions investigated during these tests were negligible.

6. Bacterial assays confirmed the expectation that the hot acid process destroys essentially all pathogens.

Bench-scale tests were also conducted with WAS to directly compare the hot acid treatment process with thermal treatment and chemical conditioning (ferric chloride and polymer addition). Thermal treatment produced the greatest improvement in sludge dewaterability. The improvement in sludge dewaterability for hot acid treatment was at least as great as for chemical conditioning. The hot acid process solubilized significant quantities of zinc, cadmium, and nickel while thermal treatment produced no significant solubilization of heavy metals, with the possible exception of nickel. On the other hand, the hot acid treatment solubilized only 8% of the COD compared to 27% for thermal treatment and solubilized only 10% of the nitrogen compared to 76% for thermal treatment. Thus the sludge from hot acid treatment should be much more desirable for land application than sludge from a thermal treatment process.

Additional bench-scale tests were conducted to define the factors responsible for solubilization of heavy metals and to optimize the hot acid process for heavy metals removal. Consistent correlations were obtained between the degree of solubilization and the acid usage in kg of concentrated H_2SO_4 per dmt. These correlations indicate a rapid increase in the degree of solubilization of cadmium, zinc, nickel, and chromium over the range of 100 to 200 kg/dmt and of copper (based on limited data) over the range of 250 to 300 kg/dmt. The correlation of metals solubilization with acid usage was found to be more consistent than correlation with pH.

Tests conducted with fresh WAS samples from various municipalities indicated excellent solubilizations of cadmium (88-100%), zinc (82-100%), and nickel (73-100%) at acid usages >200 kg/dmt. Only moderate solubilization of chromium (∿45%) was obtained, and appreciable copper solubilization (∿80%) required a higher acid usage (>300 kg/dmt). For these tests, average solids, COD, and TKN solubilizations were 24, 16, and 28%, respectively.

An acid usage of 200 kg/dmt was selected as the optimum for heavy metals solubilization. This is two to three times as great as the acid usage required for optimum dewatering (70-100 kg/dmt to achieve pH 2.5). However, the cost for acid at a usage of 200 kg/dmt is still <$10/dmt ($9/dst) and is considered to be quite acceptable for the levels of solubilization obtained.

Bench-scale and pilot-scale centrifugation tests were conducted in order to specify full-scale dewatering equipment for the hot acid process. The pilot tests indicated good cake solids concentrations (18-36% solids), but solids recoveries were low. The use of a flocculant was recommended to improve the recovery of solids.

Preliminary designs and specifications were developed for a pilot-scale and various-capacity, full-scale, hot-acid-treatment plants. For a full-scale plant with a feed capacity of 20 dmtpd (dry metric tons per day) of solids at a consistency of 3%, the total capital investment is estimated at $250,000 for hot acid treatment alone and at $647,000 for hot acid treatment plus solids separation and liquor treatment. Depending upon the amount of acid added, the process can be optimized either for dewaterability (∿100 kg/dmt) or for metals solubilization (∿200 kg/dmt). The operating and maintenance costs, including the cost of capital, for a 20 dmtpd plant are:

	Hot Acid Treatment Alone		Hot Acid Treatment, Solids Separation, & Liquor Treatment	
	$/dmt	($/dst)	$/dmt	($/dst)
Optimum Dewatering	19.00	(17.25)	29.90	(27.15)
Optimum Metals Removal	24.00	(21.79)	37.71	(34.24)

Total operating and maintenance costs, including cost of capital, were compared for various stabilization/conditioning processes: hot acid treatment, thermal treatment, anaerobic digestion, aerobic digestion, and lime treatment. The comparison did not include the cost of dewatering and supernatant (or liquor) treatment. The estimated treatment costs for a 20 dmtpd plant decreased in the order: anaerobic digestion ($74/dmt), aerobic digestion ($47/dmt), thermal treatment ($39/dmt), hot acid treatment ($19-24/dmt), and lime treatment ($16/dmt).

Based on the results of this program it is concluded that the hot acid process is a highly promising technique for the treatment of municipal sludge It has been shown that this process:

- -- substantially improves sludge dewaterability,
- -- destroys essentially all pathogens,
- -- has the potential to solubilize significant quantities of heavy metals including cadmium,
- -- preferrentially solubilizes heavy metals rather than nutrients such as organics and nitrogen, and
- -- is highly cost-competitive with alternative stabilization/conditioning processes.

SECTION 3

RECOMMENDATIONS

The bench-scale tests have indicated that the hot acid process is a highly promising technique for sludge stabilization/conditioning, and further development of the process is recommended. The next step in development of the process should be the design, fabrication, and testing of continuous-flow, transportable, pilot system similar to that described in Section 8. This system should be installed and operated at various municipal treatment plants in order to evaluate the process under dynamic flow conditions with fresh sludge.

Rather than designing and building an entire pilot system at the outset, it is recommended that only the hot acid treatment portion be built initially. Field operation of this portion of the pilot plant will permit an evaluation of the operating characteristics and control methodology for hot acid treatment. In addition, an assessment should be made of alternative techniques for dewatering the hot-acid-treated sludge and for treating the liquor remaining after separation of the solids. When the preferred techniques have been identified, the pilot system should be modified to include all unit processes and the performance of the integrated system should be demonstrated. Sufficient information should be obtained from operation of the pilot system to permit an accurate assessment of the process economics.

SECTION 4

BENCH-SCALE PROCESS STUDIES

Bench-scale tests were conducted in order to characterize and optimize the performance of the hot acid process. Specific objectives of these tests were:

-- to evaluate the process with various secondary sludges and and various mixtures of primary and secondary sludge;
-- to determine the acid requirements for the various sludges;
-- to optimize the process with respect to pH, temperature, and reaction time; and
-- to evaluate alternative solid-liquid separation techniques.

METHODS AND MATERIALS

Sludge Identification

Tests were conducted with sludge from two municipalities in eastern Massachusetts: Brockton and Fitchburg. At both locations samples of primary sludge and waste activated sludge (WAS) were obtained. Tests were conducted either with WAS alone or with an equal-volume mixture of primary and WAS. The individual sludges were stored separately and the primary WAS mixtures were prepared just before the tests in which they were used. Samples were obtained in 5-gal polyethylene carboys and refrigerated immediately upon arrival at Walden. The samples were used within 7 days of the date on which they were obtained.

Samples of Brockton waste activated sludge were obtained after dissolved-air-flotation thickening. No chemicals were added prior to the thickener. The Fitchburg waste activated sludge was obtained following dissolved-air-flotation thickening which was preceeded by the addition of polymer (Nalco 7120 or Calgon 2620). The total solids (TS) concentrations of the sludges as received were:

Sludge	Range of Total Solids (%)
Brockton WAS	2.5 - 4.9
Brockton primary & WAS	4.0 - 4.5
Fitchburg WAS	4.0 - 4.1
Fitchburg primary & WAS	4.2 - 6.8

Bench-Scale Test System

Digestion--

The system used for hot acid digestion of the sludge is shown in Figure 1. The acidified sludge was contained within a one-liter graduated cylinder wrapped with heating tape, and the power input to the heating tape was controlled by a variable transformer. The contents of the cylinder was agitated at a speed of about 60 rpm to provide good heat transfer from the walls of the container. Agitation was provided by a Phipps and Bird stirrer (Model 7790-300) which was modified for use with graduated cylinders as shown in the "Stirrer Detail" of Figure 1. A dial thermometer was attached to the shaft of the stirrer to indicate the sludge temperature. Three one-liter samples of the sludge were treated simultaneously.

Settling--

Settling tests were conducted in the same graduated cylinders as used for digestion (Figure 1). Following the digestion period the stirrers were removed from the cylinders, the power to the heating tapes was turned off, and the sludge-water interface was recorded as settling occurred.

Filtration--

The filtration test system is shown in Figure 2. Samples of treated sludge were filtered through Whatman #1 filter paper which was supported in a Buchner funnel. A tubular plexiglass extender was used to permit the entire 45 ml sludge sample to be poured into the funnel at one time. Filtrate was produced under a controlled vacuum of 51 cm (20 inches) of mercury and was collected in a 250 ml graduated cylinder.

Centrifugation--

The apparatus(8) shown in Figure 3 was used to centrifuge samples of the treated sludge. The centrifuge tube was a plastic graduated cylinder (10 ml) with the base removed, and a slot was machined in the metal tube shield. A stroboscope was used to "stop" the rotation of the centrifuge so that the interface height could be recorded as a function of time without stopping and removing the tubes. The centrifuge (Clay Adams Model 0101) was operated at 2,600 rpm which provided an average centrifugal acceleration of 750 G's.

Experimental Procedures

The refrigerated carboy containing the sludge was agitated to mix the sludge before removing samples. Three one-liter samples were placed in beakers for pH adjustment and a fourth sample was set aside for analysis. The three one-liter samples (generally adjusted to different pH's) were treated simultaneously. The pH was adjusted to the desired level by addition of concentrated (96%) reagent-grade sulfuric acid. The samples were then poured into the graduated cylinders of the apparatus shown in Figure 1 and heated to the desired temperature. The time required to heat the sludge was generally in the range of 10-20 minutes with the longer times required for

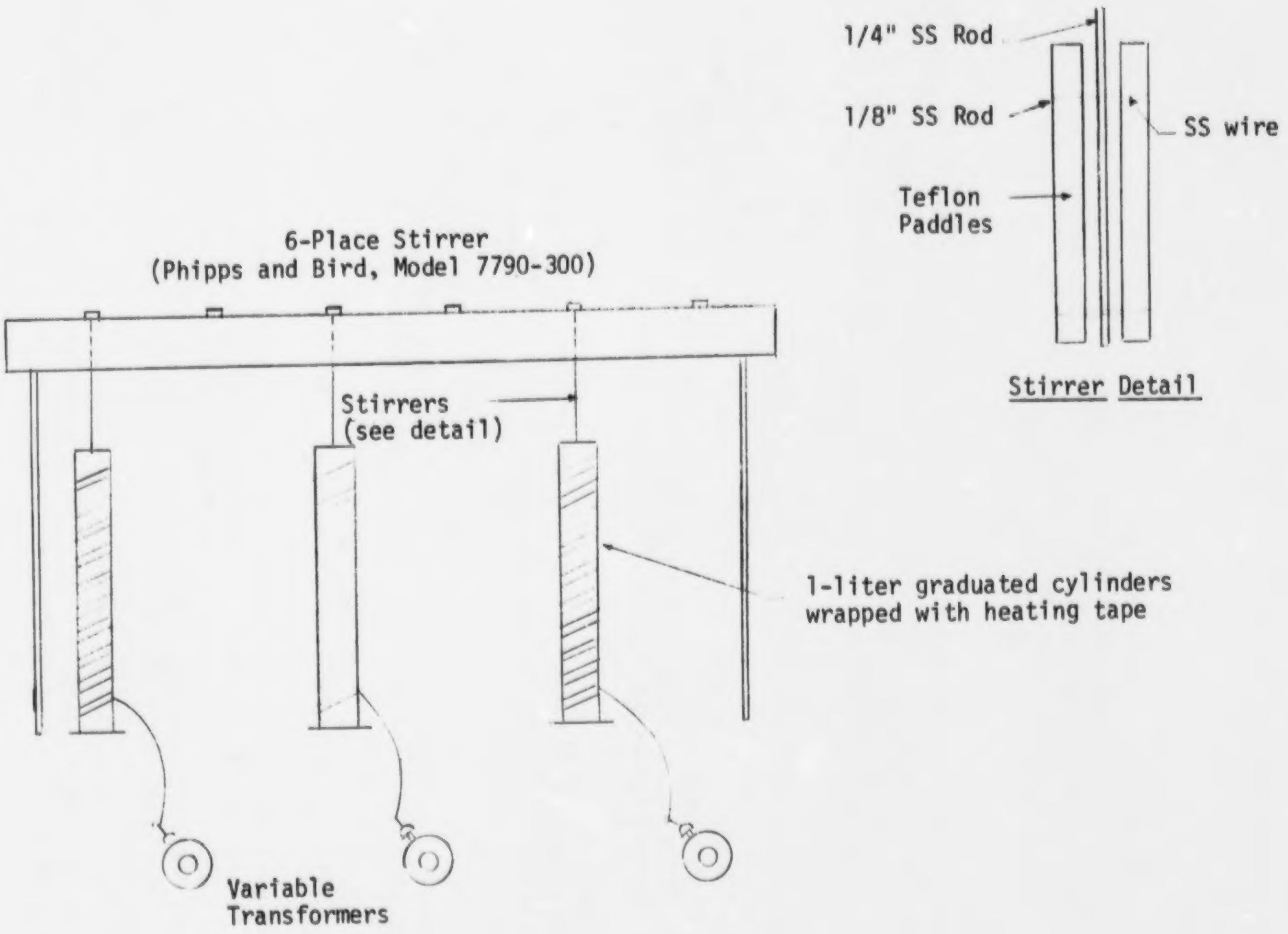
1/4" SS Rod
1/8" SS Rod
Teflon
Paddles
SS wire
Stirrer Detail
6-Place Stirrer
(Phipps and Bird, Model 7790-300)
Stirrers
(see detail)
1-liter graduated cylinders
wrapped with heating tape
Variable
Transformers

Figure 1. Digestion apparatus.

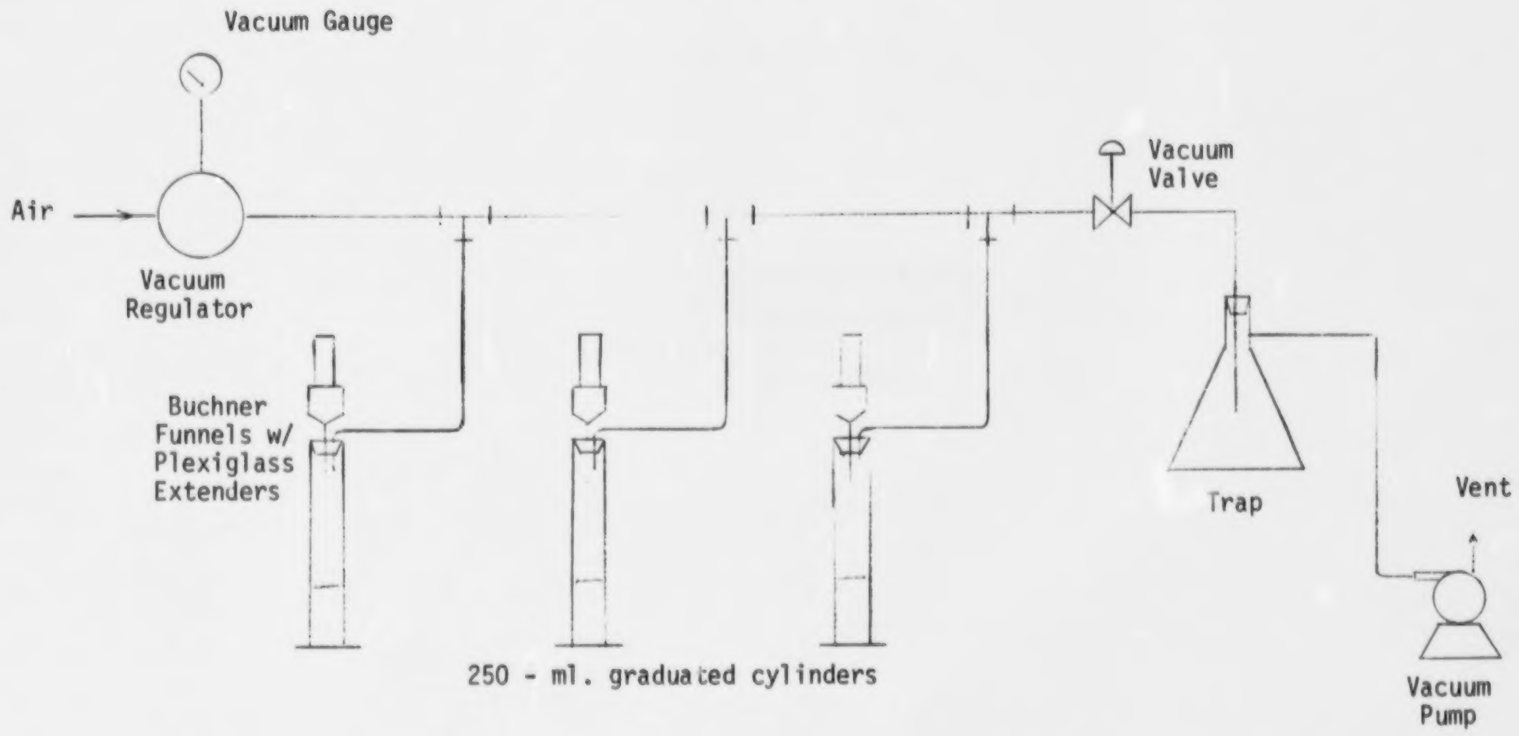
Vacuum Gauge
Air
Vacuum Regulator
Buchner Funnels w/ Plexiglass Extenders
250 - ml. graduated cylinders
Vacuum Valve
Trap
Vent
Vacuum Pump

Figure 2. Filtration test system.

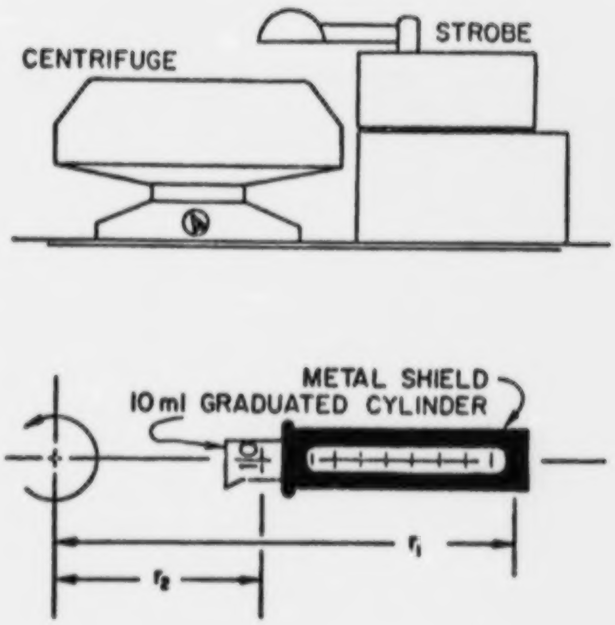
CENTRIFUGE
STROBE
METAL SHIELD
10 ml GRADUATED CYLINDER
r_1
r_2

Figure 3. Centrifugation apparatus (8).

samples exhibiting a greater tendency to foam. Samples were held at the desired temperature for the desired time by manually controlling the power input to the heating tapes.

Following digestion, 45 ml of the sludge from each of the three cylinders was poured into each of the three corresponding filters, and 10 ml from each of the three cylinders was poured into the three corresponding centrifuge tubes. The settling tests were conducted with the remaining sludge (~ 900 ml in each cylinder) by recording the interface height as a function of time over a 1-hour period. The filtration and centrifugation tests were conducted simultaneously as soon as possible after placing the samples in the respective test equipment. For filtration, the volume of filtrate was recorded as a function of time over a period of one hour, while for centrifugation, the interface height was recorded as a function of time over a period of 10 minutes.

Sampling and Analysis

Following the settling test, the contents of each graduated cylinder was thoroughly mixed and divided into two portions. One of the two portions was retained for analysis; the other was filtered through Whatman #1 filter paper, and the filtrate was retained for analysis. Similar samples (unfiltered and filtrate) of the raw sludge, which had been set aside at the outset of the test, were also retained for analyses.

The assays performed and the analytical procedures used are listed in Table 1.

Samples of sludge and sludge filtrate which had been subjected to the hot acid treatment were preserved by refrigeration prior to analysis. It was believed that the low pH of the samples (generally 2-3) along with refrigeration would sufficiently arrest any biological activity. On the other hand samples of the raw sludge were chemically preserved in addition to refrigeration. Samples for total solids analyses were preserved by the addition of formaldehyde (to 1% by weight). The formaldehyde was assumed to vaporize during evaporation of the sample prior to the gravimetric determination of total solids. Samples for COD and metal analyses were preserved by reducing the pH to 1.0 with H_2SO_4.

Data Reduction

In general the calculational procedures used in reducing the data were straight forward and require no special explanation. However, the rationale and the procedures used to calculate the percent of various sludge constituents solubilized by the hot acid process are not directly obvious and deserve further clarification. For each set of three hot-acid-treated samples, a sample of raw sludge was obtained and analyzed as the control to which the hot-acid-treated samples were to be compared. Thus for a hot-acid test at given conditions the analytical results obtained for sludge constituent M (e.g. a heavy metal or COD) were:

TABLE 1. ASSAYS AND PROCEDURES

Assay	Procedure	Reference*
Total solids	Gravimetric - total residue dried at 103°C - 105°C	SM208A
Volatile solids	Gravimetric - at 550°C	SM208E
BOD	5 day incubation, electrode	SM507
COD	Dichromate reflux	SM508
TOC	Combustion - membrane detection Dohrmann Envirotech T.O.C. Analyzer	EPA, p. 236†
Zinc	Atomic absorption	SM301A
Copper	Atomic absorption	SM301A
Cadmium	Atomic absorption	SM301A
Nickel	Atomic absorption	SM301A
Chromium	Atomic absorption	SM301A
Lead	Atomic absorption	SM301A
Total phosphorus	Persulfate digestion Ascorbic Acid Method	SM425C, 425F
TKN	Kjeldahl, selective ion electrode	EPA, p. 175†
Fecal coliform	Fecal coliform membrane filter procedure	SM909C
Fecal streptococcus	Membrane filter technic	SM910B

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[*] Standard Methods for the Examination of Water and Wastewater. Fourteenth edition. American Public Health Association, Washington, D.C. 1976.

[†] Methods for Chemical Analysis of Water and Wastes. EPA-625/6-74-003. U.S. Environmental Protection Agency, Office of Technology Transfer, Washington, D.C., 1974.

1. Total concentration of M in raw sludge (unfiltered) = $(TM)_{raw}$
2. Total concentration of M in raw sludge filtrate = $(DM)_{raw}$
3. Total concentration of M in treated sludge (unfiltered) = $(TM)_{treated}$
4. Total concentration of M in treated sludge filtrate = $(DM)_{treated}$

The concentration of suspended constituent M in the raw and treated samples is then:

$$(SM)_{raw} = (TM)_{raw} - (DM)_{raw}$$
$$(SM)_{treated} = (TM)_{treated} - (DM)_{treated}$$

The simplest procedure for calculating the percent of constituent M solubilized by the treatment process is:

$$\% \text{ Solubilized} = \frac{(SM)_{raw} - (SM)_{treated}}{(SM)_{raw}} \times 100\% \qquad (1)$$

The use of Equation (1) to calculate the percent solubilized resulted in numerous inconsistent and widely scattered results. For example, for one set of analyses the percent COD solubilized was -7% as calculated by Equation (1) even though the COD of the treated filtrate was nearly 8 times as great as the COD of the raw filtrate.

A careful inspection of the data indicated that the results calculated by Equation (1) are strongly influenced by inaccuracies in obtaining representative samples of sludge. Because of the heterogeniety of the raw sludge, two samples taken from the same container of sludge could have significantly different concentrations of suspended constituents (solids, COD, metals) although the dissolved constituents would be expected to be homogeneously distributed for all samples. These sampling-related differences in suspended constituents for two samples (one to be treated, one to remain untreated) can have a large influence on the percent solubilization calculated by Equation (1).

A second source of inaccuracy in the use of Equation (1) is that any constituents that are volatilized by the hot acid process (e.g. carbonates → carbon dioxide) are calculated as being solubilized. Thus in many cases the calculated degree of solubilization using Equation (1) indicates much higher dissolved concentrations in the filtrates than are actually present.

In order to reduce the effects of sampling inaccuracies and volatilization on the calculated percent solubilization, the amount of suspended constituent in the raw sludge was calculated from the treated sample:

$$(SM)^{*}_{raw} = (TM)_{treated} - (DM)_{raw} \qquad (2)$$

Then $(SM)^*_{raw}$ was used in Equation (1) in place of $(SM)_{raw}$. This calculational procedure gave quite consistent results, and no negative solubilizations were calculated.

The degree of suspended solids solubilization was calculated by a similar procedure except that Equation (2) was modified to take into account the sulfate added with the sulfuric acid during acidification of the sludge. Thus Equation (2) becomes:

$$(SS)^*_{raw} = (TS)_{treated} - (DS)_{raw} - (TSO_4)_{added} \qquad (3)$$

where:

$(SS)^*_{raw}$ = calculated suspended solids concentration of raw sludge

$(TS)_{treated}$ = total solids concentration of treated sludge

$(DS)_{raw}$ = dissolved solids concentration of raw sludge

$(TSO_4)_{added}$ = total concentration of sulfate added to the raw sludge

The amount of sulfate added was calculated from the known volume of concentrated H_2SO_4 added to the sample, the concentration of the acid (96%), its density (1.83 g/cc), and its $SO_4^=$ content. The concentration of suspended solids in the treated sludge was calculated by:

$$(SS)_{treated} = (TS)_{treated} - (DS)_{treated} \qquad (4)$$

No correction for sulfate is required since both the total and dissolved solids analyses for the treated sample include the added sulfate, which is assumed to remain dissolved. Equations (3) and (4) were then used in Equation (1) to calculate the percent solubilization of suspended solids.

RESULTS AND DISCUSSION

Tests were conducted to characterize and optimize the hot acid process with respect to the important performance criteria for sludge conditioning. Results are presented below for the acid requirements of the process, the solid-liquid separation rates, the solubilization of various sludge constituents, and the destruction of pathogens.

Preliminary Tests

Preliminary tests were conducted at the outset of the program in order to evaluate the effect of several process variables believed to be of minor importance and to determine the range of interest of the process variables believed to be of primary importance (pH, temperature, and digestion time). The minor process variables investigated were:

1. Stirring speed during digestion
2. Aeration during digestion
3. Concentration of H_2SO_4 added to the raw sludge

4. Sludge age and storage conditions
5. Ferric chloride or polymer addition to the treated sludge.

The ranges of major process variables investigated were:

pH	1.5 - 4.0
Digestion Temperature	80 - 95°C
Digestion Time	10 - 60 minutes

All preliminary tests were conducted with Brockton WAS using the procedures described above. Unless otherwise specified, the minor process variables were investigated at a pH of 2, a temperature of 95°C, and a digestion time of 30 minutes.

Stirring Speed During Reaction--

Different stirring speeds were investigated during digestion to determine if the stirring speed affects the solid-liquid separation rate or the degree of TOC solubilization. Two samples of sludge were acidified to pH 2 and digested at 95°C for 30 minutes using a stirring speed of 60 rpm. One of the samples was then subjected to high shear by mixing in a Waring blender for two minutes.

Settling curves for the two samples are shown in Figure 4. The height of the interface (as indicated by the ml graduations on the graduated cylinder) is plotted as a function of settling time. The sample subjected to high shear settled much slower than the sample subjected to low shear. This suggests that flocs formed during digestion may have been broken up by the intense mixing in the blender.

Since homogenization is used in many biological investigations to induce lysis of cellular materials, it was anticipated that high-shear mixing would increase the TOC of hot-acid-treated sludge. However, the TOC of the filtrate of the high-shear sample (1140 mg/l) was slightly lower than the TOC of the filtrate of the low-shear sample (1250 mg/l). This indicates that cell lysis was not significant at the stirring speeds used. It was concluded that the stirring speed should be adjusted to the minimum speed that maintains a reasonably uniform temperature profile throughout the sludge during digestion. In all subsequent tests with this apparatus a stirring speed of 60 rpm was used. (Tests at a higher stirring speed using a different apparatus are described in Section 6).

Aeration During Reaction--

Aeration during digestion was investigated to determine whether or not it had any effect on the solids separation rate or the degree of TOC solubilization. Two samples were digested at identical conditions except that oxygen was sparged into one of the samples during digestion.

The settling curves are shown in Figure 5 for both the oxygen-sparged sample and the control. The oxygen-sparged sample settled more slowly than the control. This may be the result of oxygen-entrainment in the sparged sludge which would reduce its density and inhibit settling.

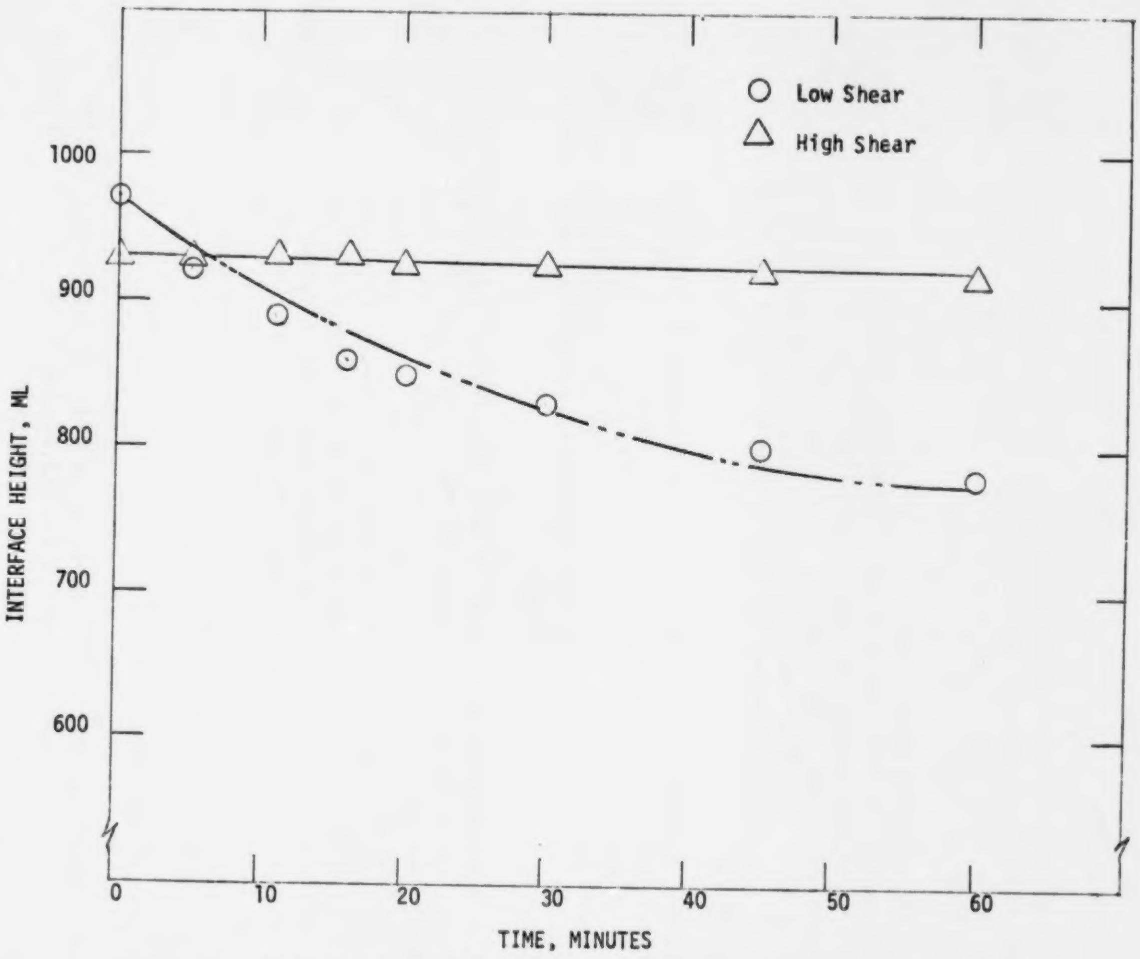

Figure 4. Effect of stirring speed during digestion on the settling rate of hot-acid treated WAS.

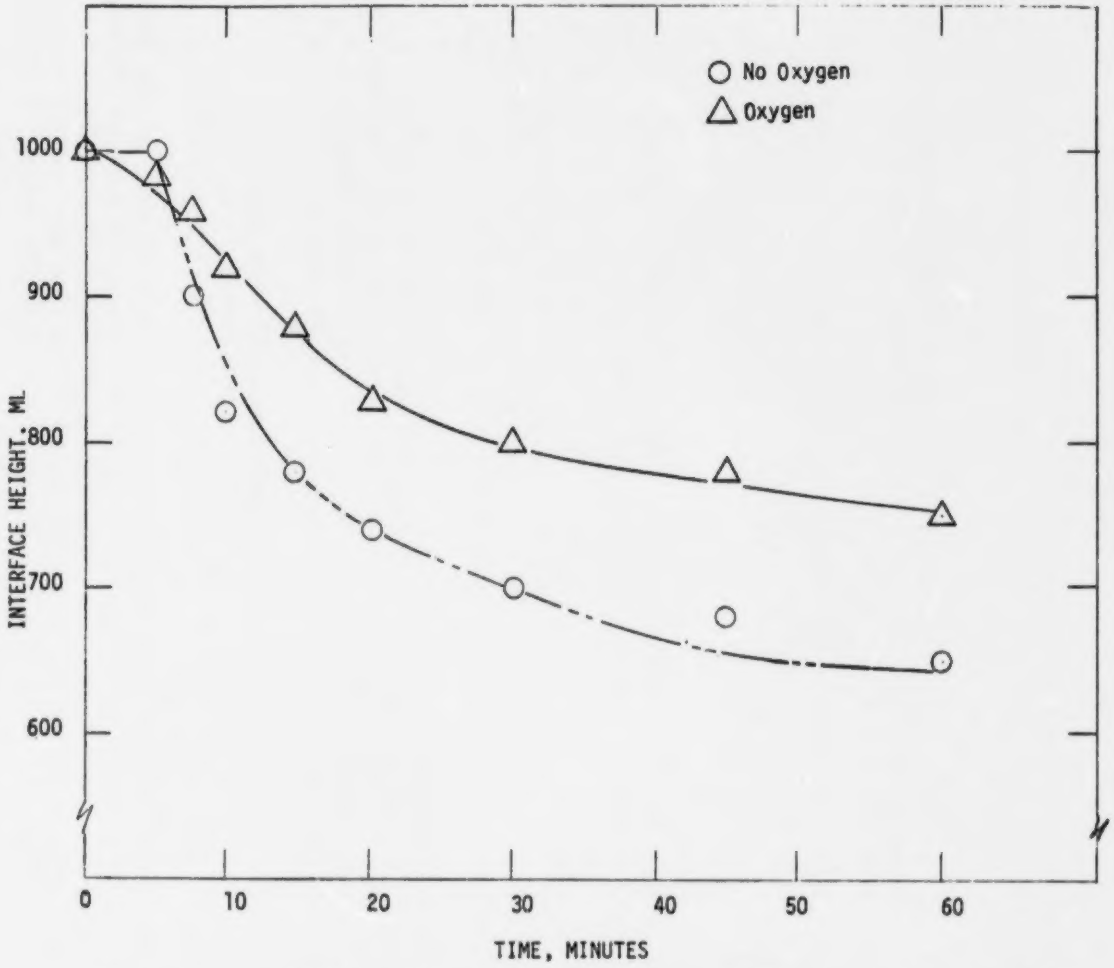

Figure 5. Effect of oxygen sparging during digestion on the settling rate of hot-acid-treated WAS.

There was no significant difference in the concentrations of soluble TOC for the two samples (1500 mg/l for the oxygen-sparged sample, 1540 mg/l for the control).

Based on these results, air sparging would appear to have no beneficial effects on the hot-acid process. The evaluation of air sparging to improve the solubilization of heavy metals is considered in Section 6.

Concentration of Sulfuric Acid--

The effect of acid concentration of process performance was investigated using three different acid concentrations:

1. concentrated H_2SO_4 (96% by weight)
2. concentrated H_2SO_4 diluted with an equal volume of water (50:50)
3. concentrated H_2SO_4 diluted with three times its volume of water (25:75)

Settling curves are shown in Figure 6 for digested samples acidified with the three different concentrations of acid. The samples treated with the two higher acid concentrations gave similar settling curves, and, except for the last 15 minutes of the test, both settled more rapidly than the 25:75 sample.

The effect of the concentration of added acid on the solubilization of organics (here, measured as soluble TOC) was investigated. The TOC values of the filtrates for the concentrated 50:50 and 25:75 concentrations were 1760, 1850, and 2120 mg/l, respectively. This is interesting, since it was expected that the higher concentrations would solubilize more organics. Although the explanation of this behavior is not apparent, it can be concluded that concentrated acid should be used in the process.

Sludge Age and Storage Conditions--

Sludge age and storage conditions were investigated in order to determine whether a new supply of sludge was required each day, or whether sludge could be stored for a certain period of time without significant deterioration with respect to evaluating process performance.

The three storage conditions examined were: 1) room temperature (biologically active sludge), 2) formaldehyde treatment, 1% by volume (biologically inactive), and 3) refrigeration (biologically arrested).

Each working day during a six-day period, a sample of each of the three sludges was acidified and digested, and settling curves, as well as TOC and solids data, were generated. The interface height after 30 minutes of settling time is shown below as a function of sludge age and storage condition. (The interface height is given in terms of the volume of sludge remaining out of an initial volume of 1000 ml.)

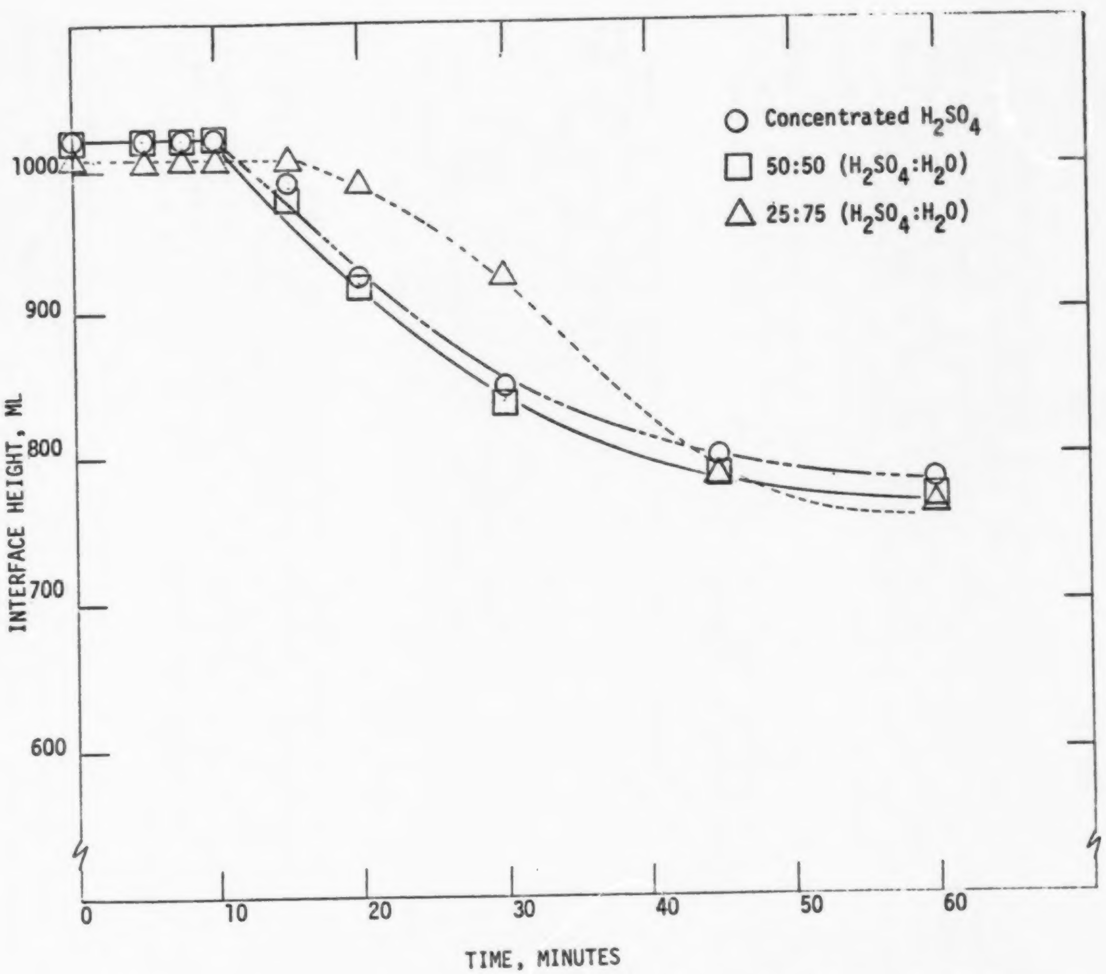

Figure 6. Effect of the concentration of added acid on the settling rate of hot-acid-treated WAS.

Time (days)	Sludge volume remaining after 30 minutes of settling (ml)		
	Room temperature	Refrigerated	Formaldehyde
0.25	810	810	920
1.1	760	700	815
4	810	820	960
5	820	790	930
6	820	790	930

From these data it is apparent that the room temperature and refrigerated samples settle at approximately the same rate after hot acid treatment, but the formaldehyde-treated sample settles significantly slower following hot acid treatment. This result rules out the use of formaldehyde for sludge preservation. Comparing the settling rates observed on the first day with those observed on the sixth day, the results appear to lie within the experimental precision of the test.

The pH of the sludge was measured each day during storage and is shown in Figure 7. The curves all have the same general shape and indicate a decrease in pH with storage time. The pH change -- from 6.0 to 5.5 over six days -- is considered tolerable.

The soluble TOC concentrations of the three sludge samples are shown in Figure 8 as a function of storage time. The soluble TOC of the refrigerated sludge remained fairly constant throughout the six-day period (160 mg/l ± 25), while both the HCHO-treated and room-temperature sludges showed constant increases in soluble TOC (80 and 60 mg/l-day, respectively). These increases may be due either to cell autolysis which occurs during endogenous respiration (in the case of room-temperature sludge) or to the loss of cell membrane semi-permeability (in the case of the HCHO-treated sludge). The TOC values for the HCHO-treated sludge are much larger than the values for the other two sludges because the formaldehyde contributes to the total organic carbon concentration.

The total solids and dissolved solids concentrations of the three sludge samples are shown as a function of sludge age in Table 2. Although there is some variability in the total solids analyses, there is no consistent trend to higher or lower total solids concentrations with storage time. The scatter in the total solids data is probably the result of the heterogeniety of the sludge which made it difficult to obtain a truely representative sample.

The dissolved solids in the raw sludge account for only about 5% of the total solids. There appears to be a consistent increase in dissolved solids during the first day of storage, but thereafter the dissolved solids concentrations remain reasonably constant. The scatter in the dissolved solids data could be the result of analytical errors since only a rather small volume of sample was submitted for analysis.

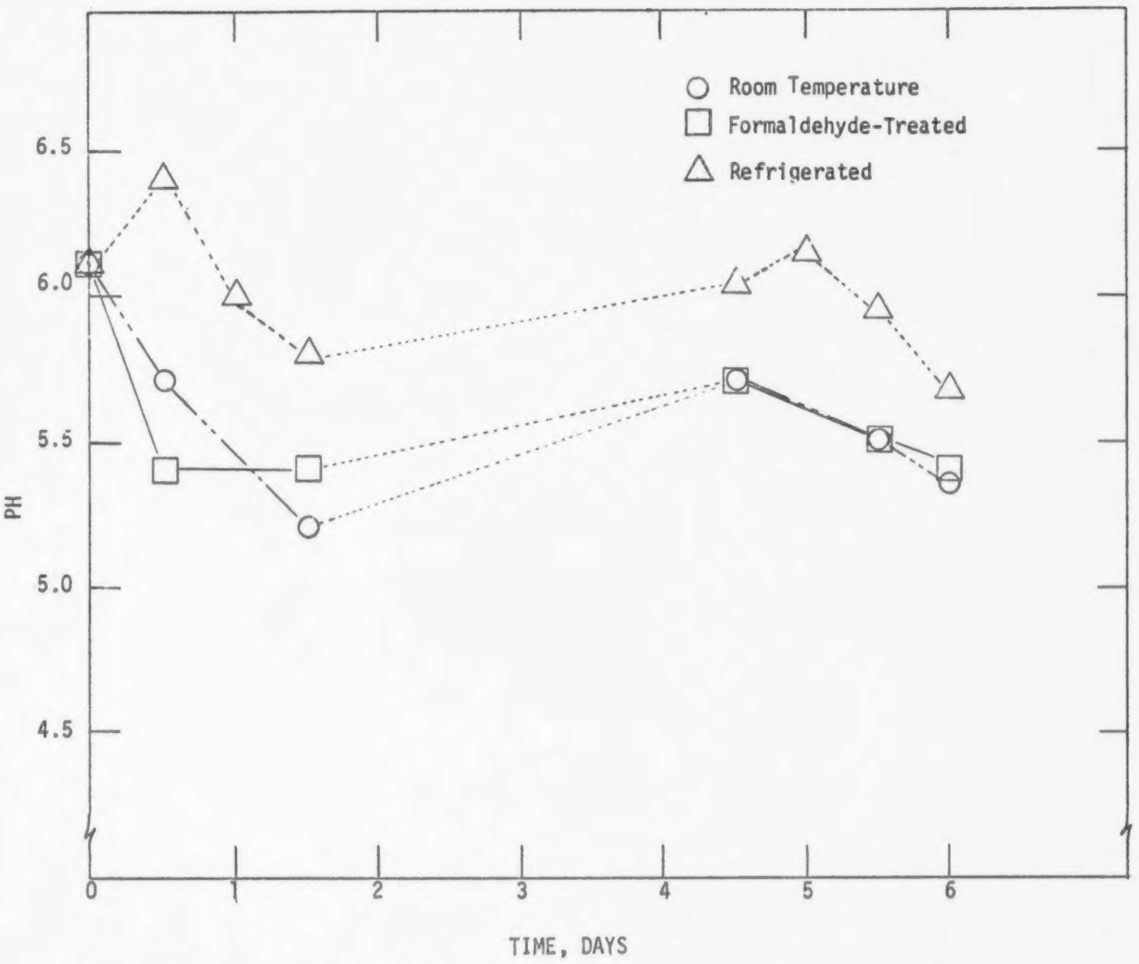

Figure 7. Variation of WAS pH with time for various storage conditions.

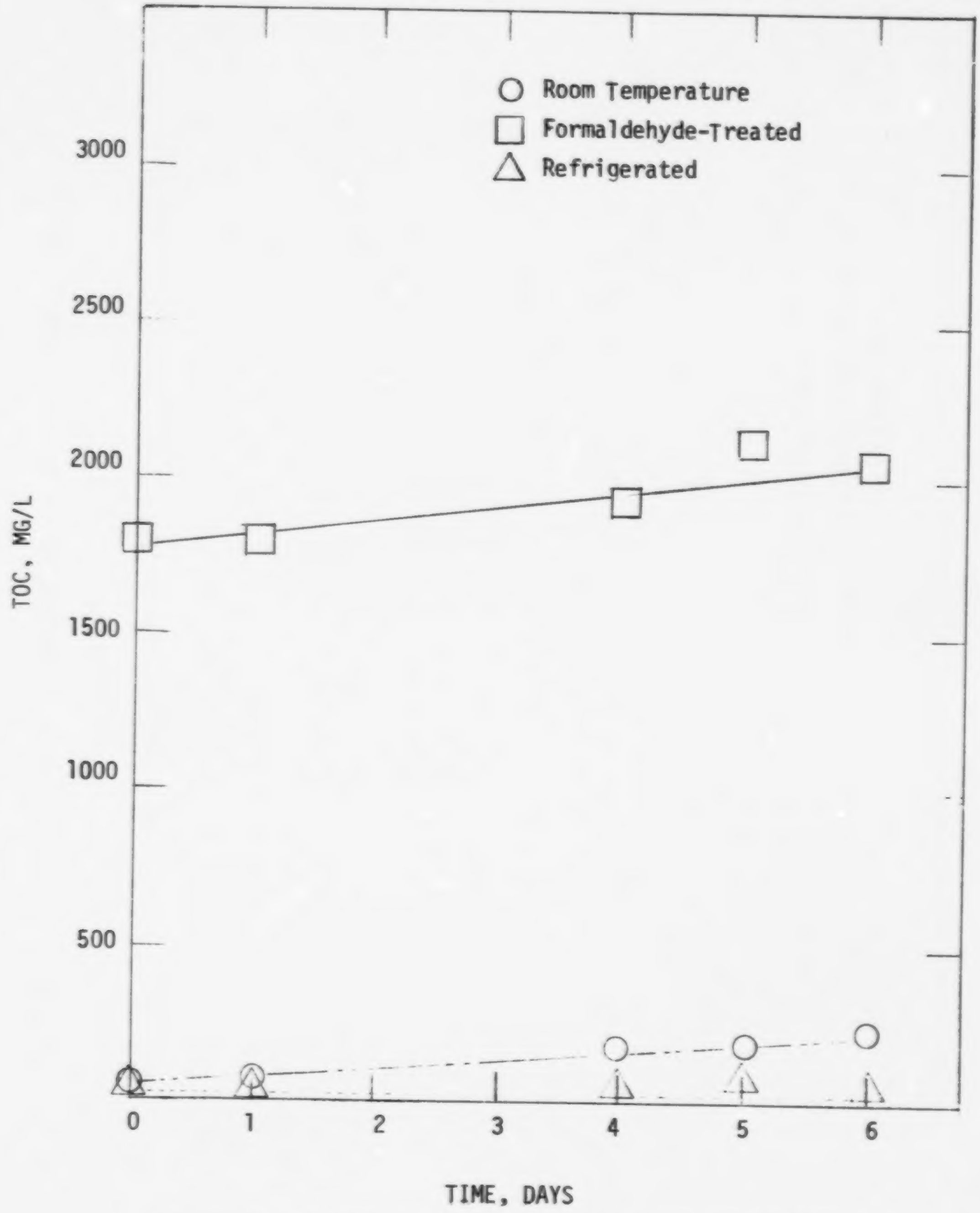

Figure 8. Variation of WAS TOC with time for various storage conditions.

TABLE 2. SOLIDS CONCENTRATIONS AS A FUNCTION OF SLUDGE AGE AND STORAGE CONDITIONS

Storage condition	Sludge age (days)	Total solids (mg/1)	Dissolved solids (mg/1)
Room temperature	0	27,800	802
	1	28,100	1,190
	4	27,500	1,710
	5	27,200	1,190
	6	27,500	1,340
Refrigerated	0	28,600	434
	1	29,000	872
	4	29,100	944
	5	26,500	1,220
	6	28,000	1,170
Formaldehyde	0	28,300	384
	1	28,500	866
	4	29,800	1,030
	5	27,600	1,020
	6	27,400	976

Ferric Chloride or Polymer Addition--

Ferric chloride and various polymers were evaluated to determine whether or not their use in conjunction with the hot acid process would produce a substantial improvement in the solid-liquid separation rates. For each set of tests three samples were compared: the first was hot acid treated without additives, the second was hot acid treated with the additive added before digestion, the third was hot acid treated with the additive added after digestion. Ferric chloride was added as a 10%-by-weight solution in sufficient quantity to reduce to pH of the raw sludge to 3.0. Several types of acrylamide-based polymers were evaluated (Allied Colloids' Percol 720, 725, 726, and 728) each at a dosage of 50 ppm based on the weight of the wet sludge.

It was concluded on the basis of settling, filtration, and centrifugation tests that the addition of ferric chloride or polymer at the conditions investigated did not substantially improve the solid-liquid separation rates for the hot acid process. Although minor improvements were observed in some cases, the improvements were not considered sufficient to justify the additional cost of the additive.

Selection of Ranges for Major Process Variables--

Tests were conducted to identify the ranges of pH, temperature, and time for which the hot acid process produced the best performance. The pH was studied over a range of 1.5-4.0; the temperature, over a range of 80-95°C; and the time, over a range of 10-60 minutes. For the tests at various pH 's all samples of Brockton waste activated sludge (2.7% solids) were digested at 95°C for 30 minutes. The settling, filtration, and centrifugation curves are shown in Figures 9, 10, and 11, respectively. For settling the interface height (calculated as the percent of initial sludge volume remaining) is plotted against settling time. The sludge samples digested at pH 2.5 settled most rapidly followed by the sludge settled at pH 2.0. For filtration (Figure 10) the volume of filtrate collected out of an initial volume of 45 ml is plotted against filtration time. The sludge samples digested at pH 2.5 and 3.0 filtered the most rapidly. For centrifugation the interface height (calculated as the volume of sludge remaining from an initial volume of 10 ml) is plotted against the centrifugation time. The sample adjusted to pH 4 centrifuged least rapidly, but all of the other samples appeared to centrifuge at about the same rate. Based on these tests it was concluded that the optimum pH range for the hot acid process is 2.0 to 3.0.

Tests conducted at temperatures of 80, 90, and 95°C (at pH 1.5 and 45 min digestion time) indicated better solid-liquid separation at a digestion temperature of 95°C. Since higher temperatures are ruled out by the boiling point of water and lower temperatures give lower solid-liquid separation rates, it was concluded that the optimum temperature range for solid-liquid separation is 80-95°C.

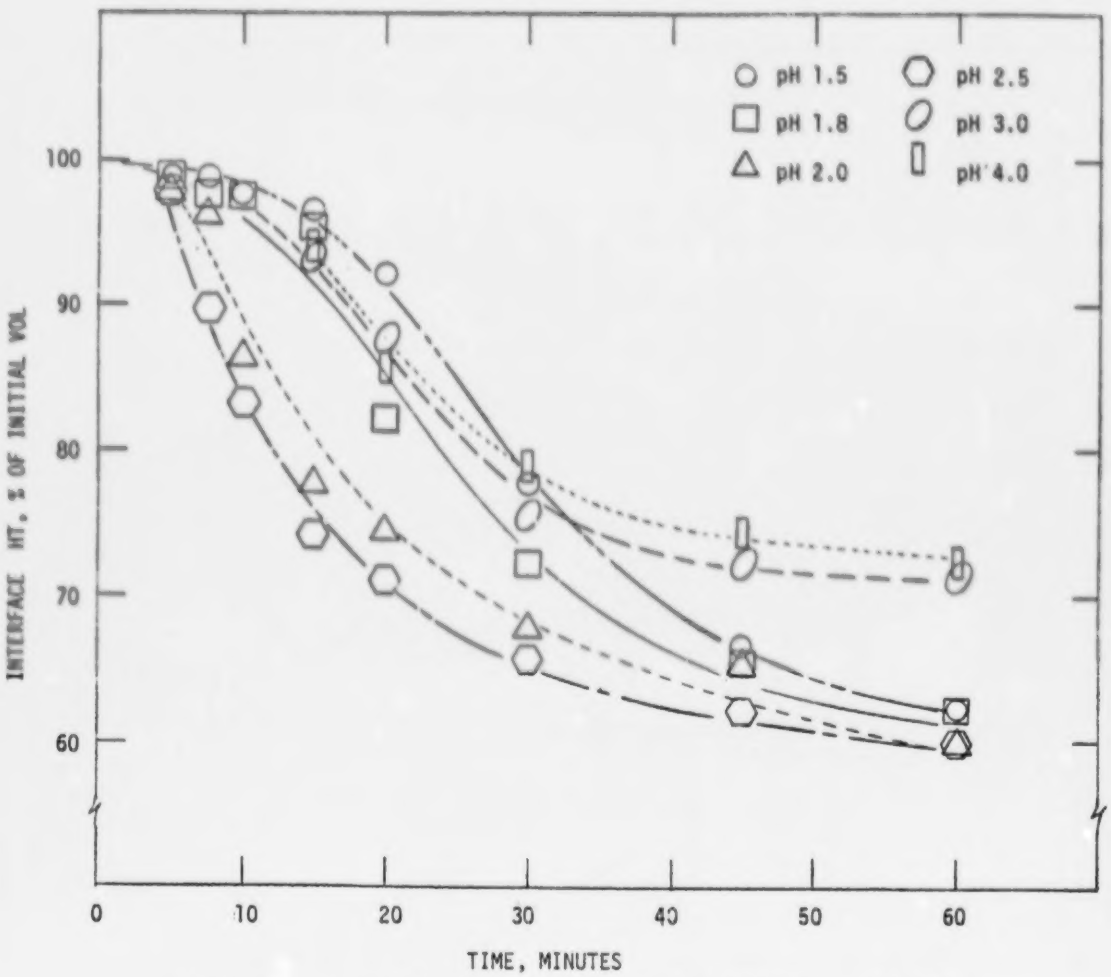

Figure 9. The effect of pH on the settling rate of WAS digested at 95°C for 30 minutes.

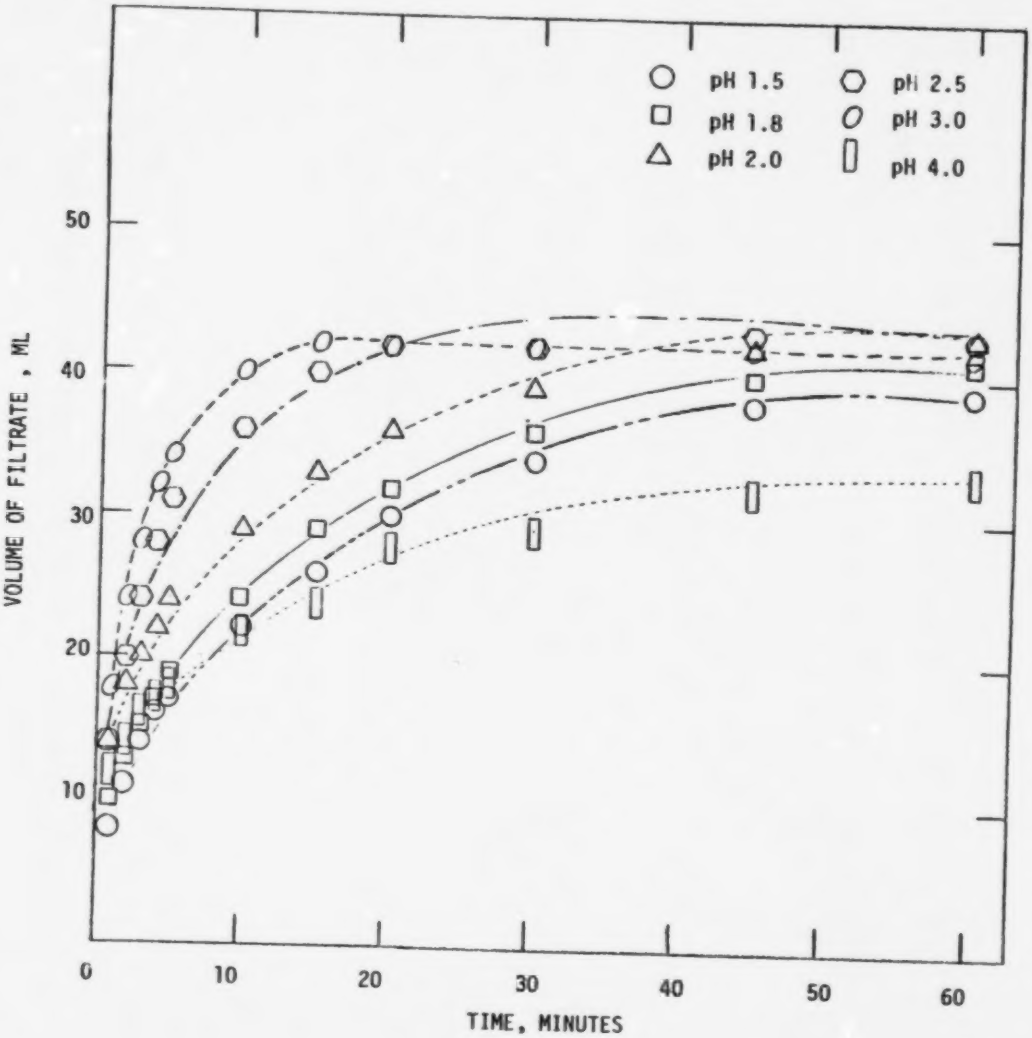

Figure 10. The effect of pH on the filtration rate of WAS digested at 95°C for 30 minutes.

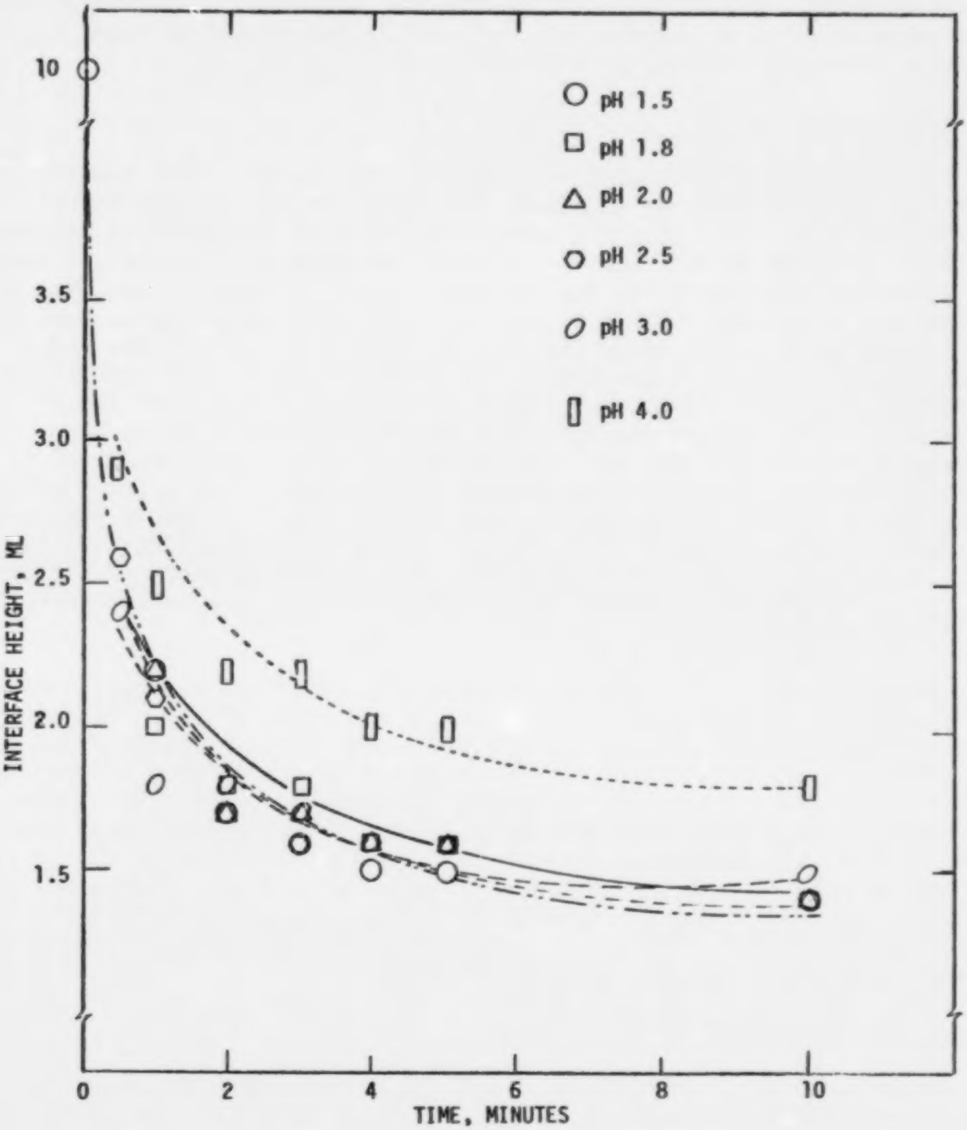

Figure 11. The effect of pH on the centrifugation rate of WAS digested at 95°C for 30 minutes.

Two different sets of tests were conducted to evaluate the variable of time. In the first, three samples were digested at pH 1.5, a temperature of 95°C and times of 30, 45, and 60 minutes, respectively. In the second set, three samples were digested at pH 2.5, a temperature of 95°C, and times of 10, 20, and 30 minutes, respectively. From these tests the solid-liquid separation rates did not appear to be strongly dependent on digestion time, and a range of 10 to 60 minutes was selected as the preferred range of digestion times for the hot acid process.

Acid Requirements

Concentrated sulfuric acid was added to the sludge before heating, and the volume of acid required to adjust the sludge to the desired pH was recorded for each test. Table 3 summarizes the acid requirements determined during the program for the tests of primary importance. A series of tests were conducted with the first four sludges listed in Table 3 resulting in 9 separate tests for each sludge at each pH. The acid requirements were calculated both on a solids basis (kg acid per metric ton of solids) and on a wet sludge basis (kg acid per metric ton of wet sludge). For each sludge at a given pH, the acid requirement should be the same for each of the 9 tests. In general, there is some scatter about the mean as indicated by the standard deviation, but the standard deviation (relative to the mean) is consistently less when the acid requirement is calculated on a wet sludge basis rather than a sludge solids basis. This implies that the liquid fraction of the sludge exerts a greater acid demand than the solid fraction. On the other hand, comparison of the acid requirements for sludges obtained on different dates (e.g. results for Brockton WAS at pH 1.5) suggests a better correlation on a sludge solids basis.

Figures 12 and 13 present the average acid demand as a function of pH on a sludge solids basis and a wet sludge basis, respectively. The points in each figure indicate the average of the means listed in Table 3 for the indicated pH. (In calculating this average all means of Table 3 were weighted equally even through some means are more uncertain than others.) The relationship between acid demand and pH is approximately linear over the range of pH 2 to 3 but begins to increase rapidly below a pH of 2. It is of interest to note that at pH 2.0 the acid demand of all the sludges are about the same. At this pH the approximate acid requirement is 110 kg/dmt solids or 4.4 kg/ wmt sludge. Of the sludges tested the Fitchburg WAS required the most acid to achieve the desired pH levels.

Solid-Liquid Separation

For each of the four sludges, a full-factorial experimental design was used to evaluate the effects of the major process variables (pH, temperature, and time) on solid-liquid separation and on solubilization of various sludge constituents. In the full-factorial design, all combinations of the three "factors" (pH, temperature, and time) at each of three levels (27 tests per sludge) were tested. The levels investigated were:

TABLE 3. ACID REQUIREMENTS AS A FUNCTION OF PH FOR BROCKTON AND FITCHBURG SLUDGES

Sludge sample [a]	n	Total solids[b] (% by weight)		pH	Number of tests	H_2SO_4 added (mℓ/ℓ)		Acid required [d] (kg/dmt solids)		Acid required [d] (kg/wmt sludge)	
		Mean	Std. dev.			Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
B-2° (2-28)	9	4.21	0.51	2.0	9	2.38	0.15	100	15.2	4.18	0.26
				2.5	9	1.68	0.26	70.9	15.7	2.95	0.46
				3.0	9	0.87	0.09	36.6	5.5	1.52	0.15
F-2° (3-15)	9	4.02	0.16	2.0	9	2.57	0.07	112	5.5	4.51	0.12
				2.5	9	1.94	0.05	84.8	3.8	3.42	0.09
				3.0	9	1.07	0.17	46.6	7.6	1.88	0.29
B-1°+2° (3-28)	9	4.53	0.42	2.0	9	2.48	0.04	98.8	7.4	4.35	0.07
				2.5	9	1.90	0.00	74.1	6.3	3.34	0.00
				3.0	9	0.90	0.00	35.1	3.0	1.58	0.00
F-1°+2° (4-11)	9	4.22	1.18	2.0	9	2.43	0.07	112	43.5	4.28	0.12
				2.5	9	1.91	0.03	87.9	34.2	3.36	0.06
				3.0	9	0.82	0.07	38.7	10.2	1.44	0.12
B-2° (2-14)	6	3.98	0.19	1.5	7	4.23	0.21	186	2.1	7.43	0.37
				2.0	10	2.26	0.14	101	3.4	3.97	0.24
				2.5	1	2.0	--	82.5	--	3.51	--
B-2° (2-22)	3	2.53	0.22	1.5	2	2.2	0.00	219	7.0	5.80	0.00
				1.8	1	2.4	--	156	--	4.22	--
				2.0	1	1.8	--	117	--	2.99	--
				2.5	4	1.2	0.00	92.2	0.0	2.11	0.00
				3.0	1	0.7	--	53.8	--	1.23	--
				4.0	1	0.5	--	38.4	--	0.88	--
B-2° (4-26)	3	3.53	0.95	2.0	1	2.7	--	156	--	4.74	--
				2.3	1	2.2	--	128	--	3.86	--
				2.5	2	1.65	0.07	78.7	14.2	2.90	0.13
				2.6	1	1.3	--	78.0	--	2.28	--
				2.8	1	1.0	--	60.0	--	1.76	--
				3.0	1	0.9	--	54.0	--	1.58	--
F-2° (5-10)	2	4.06	0.05	2.0	1	2.8	--	120	--	4.92	--
				2.3	1	2.6	--	112	--	4.57	--
				2.5	1	2.4	--	103	--	4.22	--
				2.6	1	2.2	--	96.2	--	3.86	--
				2.8	1	2.0	--	87.4	--	3.51	--
				3.0	1	1.8	--	78.7	--	3.16	--
B-1°+2° (5-3)	2	4.11	0.24	2.0	1	2.5	--	111	--	4.39	--
				2.3	1	2.0	--	89.2	--	3.51	--
				2.5	1	1.6	--	71.4	--	2.81	--
				2.6	1	1.3	--	53.4	--	2.28	--
				2.8	1	1.1	--	45.2	--	1.93	--
				3.0	1	0.9	--	36.9	--	1.58	--
B-2° (5-19)	1	3.21	--	2.5	1	1.8	--	98.5	--	3.16	--
B-2° (5-26)	1	2.51	--	2.5	1	1.8	--	12.6	--	3.16	--
B-1°+2° (5-27)	1	4.00	--	2.5	1	1.9	--	83.4	--	3.34	--
F-2° (6-3)	1	4.06	--	2.5	1	2.2	--	95.2	--	3.86	--
F-1°+2° (6-7)	1	6.78	--	2.5	1	2.3	--	59.6	--	4.04	--
B-2° (8-17)	1	4.90	--	1.0	1	13.5	--	484	--	23.7	--
				1.2	1	10.3	--	369	--	18.1	--
				1.5	1	5.5	--	197	--	9.66	--
				2.0	1	3.2	--	115	--	5.63	--
				2.5	1	2.3	--	82.5	--	4.04	--

a. Sludge identification; example: B-1°+2° (3-28) stands for Brockton primary plus secondary sludge (WAS) obtained on February 28, 1977.

b. Total solids concentration of raw sludge. n = number of independent sample/analyses on the sludge, mean = arithmetic average, Std. Dev. = standard deviation.

c. Gives the mℓ of 96% H_2SO_4 added to 1 liter of sludge.

d. Acid requirement calculated on a 100% H_2SO_4 basis per dry metric ton (dmt) or wet metric ton (wmt).

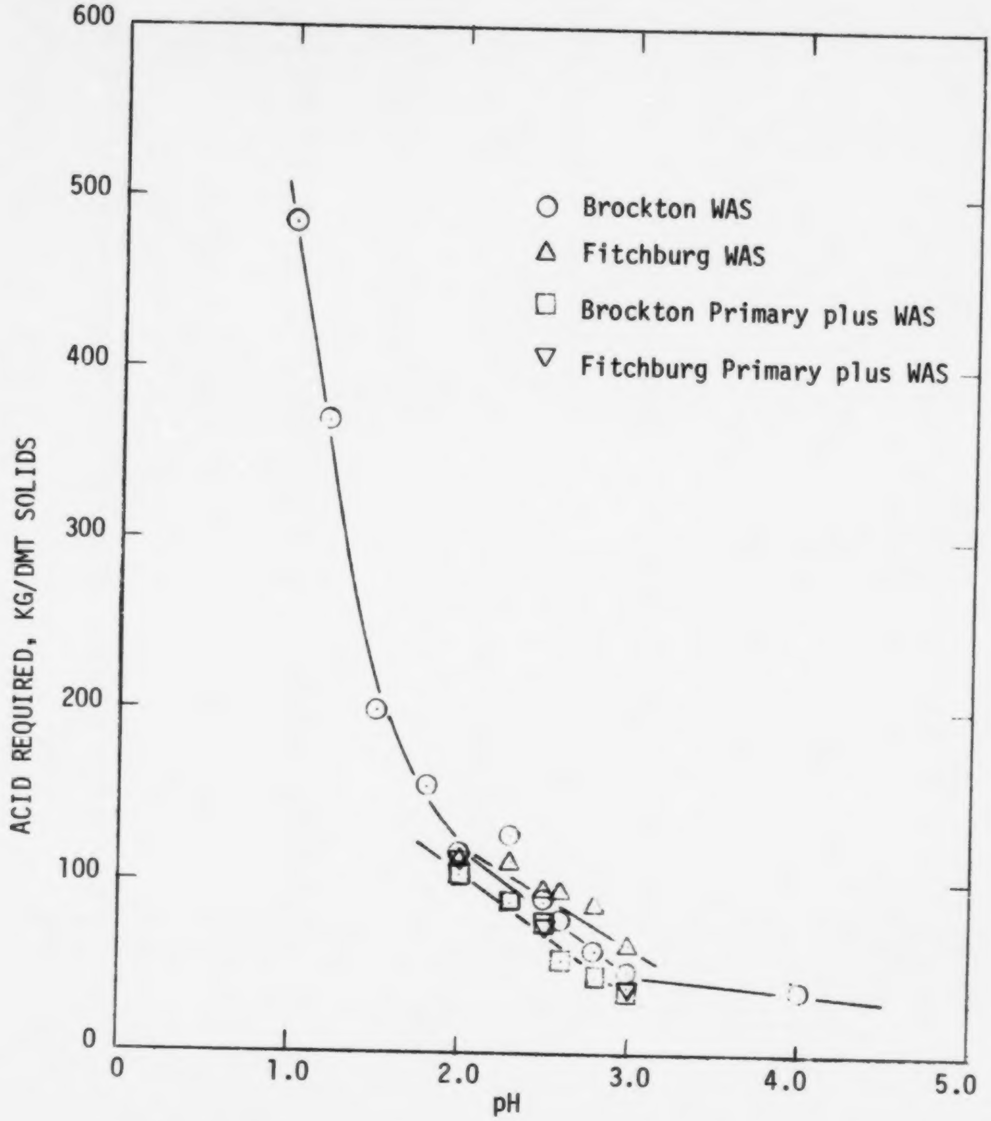

Figure 12. Acid demand vs. pH for various sludges (sludge solids basis).

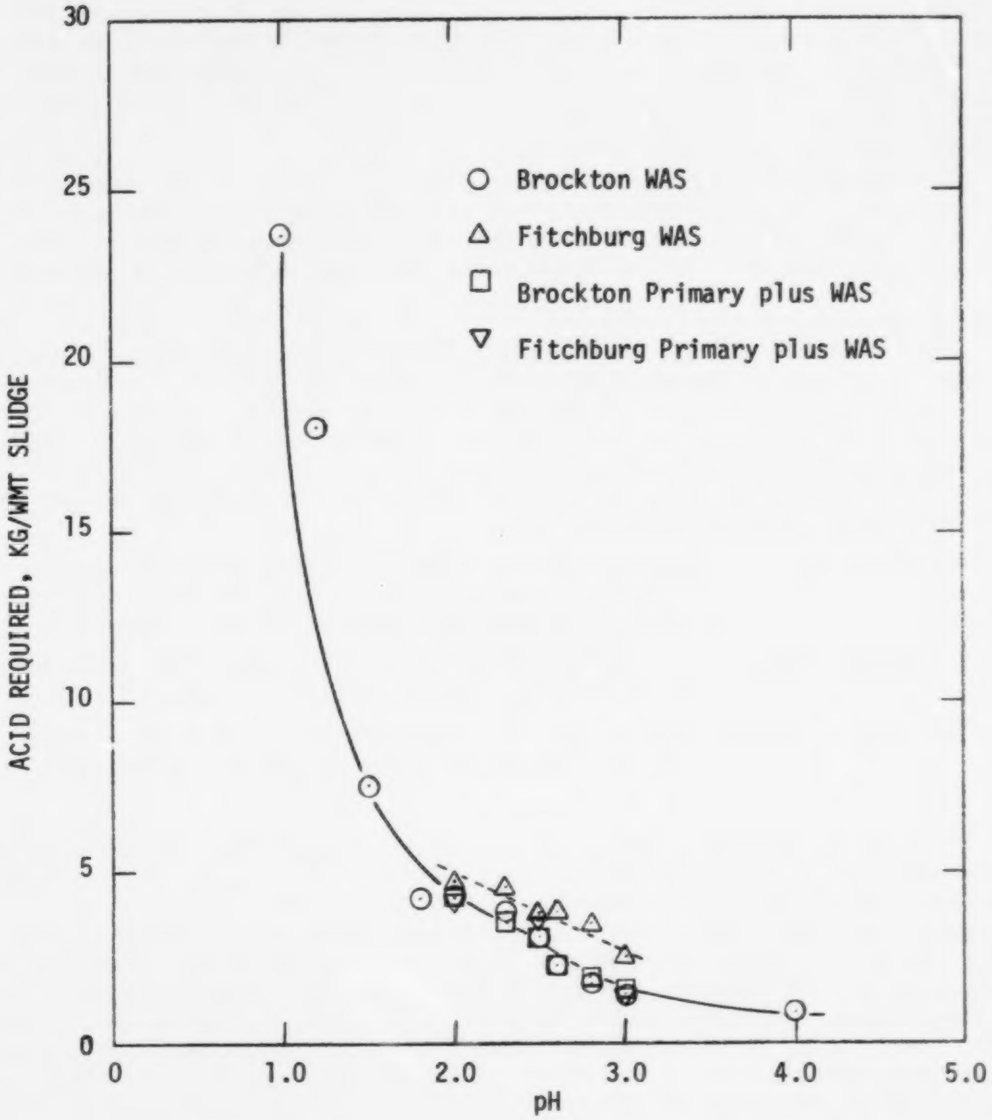

Figure 13. Acid demand vs. pH for various sludges (wet sludge basis).

pH	2.0, 2.5, and 3.0
Temperature	80, 90, and 95°C
Time	10, 30, and 60 minutes

These levels were selected on the basis of the preliminary tests described above. For the most part, all of the 27 tests for a particular sludge were completed within one week in order to limit the extent of changes in the nature of the sludge. In addition, the order in which the variables were investigated was randomized so that if the age of the sludge had an effect on performance, the effect would not be misinterpreted as arising from the variation of one of the factors being investigated. The test matrix for the optimization tests is given in Table 4. In general, a fresh sample of sludge was obtained on Monday morning, and the first set of tests was conducted in the afternoon. On subsequent days, two sets of tests were conducted. For each set, three samples, adjusted to the three different pH levels, were digested simultaneously at the temperature and time indicated in Table 4.

Brockton Waste Activated Sludge--

Table 5 gives the results for solid-liquid separation rates following hot-acid treatment of Brockton WAS. As indicated in Table 3, the average total solids content of this sludge was 4.21 % by weight. Because of the large number of tests, it is not feasible to present rate curves for each test and each solid-liquid separation technique. Instead, the rates of solid-liquid separation are indicated in Table 5 by a single parameter for each technique. These parameters are:

for settling: the volume of sludge remaining after 30 minutes settling time (calculated as a percentage of the initial volume of sludge which was ~ 900 ml).

for filtration: the volume of filtrate collected after 20 minutes of filtration (from an initial volume of 45 ml).

for centrifugation: the volume of sludge remaining after 10 minutes of centrifugation (from an initial volume of 10 ml).

In order to determine which factors have a significant influence on the solids separation rate, a 3-way, 3-level analysis of variance was performed using standard statistical techniques (9). The "F-Test" was used to determine, with 95% confidence, whether or not there was a difference in solids separation rates at different levels of a given factor. The results of the analysis of variance for solids separation are shown in Table 6. The first column gives the main effect or interaction for which the variance of test results is to be analyzed. The three-way interaction between time, temperature, and pH was assumed to be negligible and was therefore used as an estimate of the experimental error. For each solids separation technique the test F, calculated from the experimental data, and the tabulated F for the 95% confidence level ($F_{0.95}$) are given. If the test F is greated than $F_{0.95}$ the main effect or interaction is significant. The third column under each solids separation technique indicates whether the factor (or interaction) is significant ("yes") or not ("no").

TABLE 4. TEST MATRIX FOR EVALUATION OF PRIMARY VARIABLES

Day	Test set	Time (min.)	Temp. (^{o}C)	pH
Mon.	1	10	80	2.0, 2.5, 3.0
Tues.	2	30	90	2.0, 2.5, 3.0
	3	60	95	2.0, 2.5, 3.0
Wed.	4	30	80	2.0, 2.5, 3.0
	5	60	90	2.0, 2.5, 3.0
Thurs.	6	10	95	2.0, 2.5, 3.0
	7	60	80	2.0, 2.5, 3.0
Fri.	8	10	90	2.0, 2.5, 3.0
	9	30	95	2.0, 2.5, 3.0

TABLE 5. EFFECT OF TREATMENT CONDITIONS ON SOLID-LIQUID SEPARATION RATES FOR BROCKTON WAS

TREATMENT CONDITIONS			SOLIDS SEPARATION RATES		
Time (min.)	Temp (°C)	pH	Settling 30-min sludge vol., %	Filtration 20-min filtrate vol., ml	Centrifugation 10-min sludge vol., ml
10	80	2.0	95.7	20	3.0
		2.5	100	28	2.8
		3.0	100	16	3.5
	90	2.0	83.1	23	2.4
		2.5	90.0	26	2.4
		3.0	98.2	20	2.8
	95	2.0	82.2	28	2.5
		2.5	86.7	29	2.8
		3.0	98.3	16	2.9
30	80	2.0	99.2	18	2.9
		2.5	99.2	22	3.0
		3.0	100	15	3.4
	90	2.0	88.8	20	2.7
		2.5	93.2	32	2.5
		3.0	100	17	3.3
	95	2.0	87.8	27	2.4
		2.5	84.3	32	2.3
		3.0	100	18	2.7
60	80	2.0	91.2	20	2.9
		2.5	97.8	25	2.9
		3.0	100	14	3.4
	90	2.0	97.9	24	2.8
		2.5	99.2	28	2.6
		3.0	100	17	3.6
	95	2.0	91.1	28	2.5
		2.5	88.9	33	2.5
		3.0	100	18	2.9

TABLE 6. ANALYSIS OF VARIANCE RESULTS FOR SOLIDS SEPARATION TESTS (BROCKTON WASTE ACTIVATED SLUDGE)

Source of variation	Settling			Filtration			Centrifugation		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?
Time	1.76	4.46	NO	2.67	4.46	NO	2.00	4.46	NO
Temperature	10.44	4.46	YES	13.33	4.46	YES	18.00	4.46	YES
pH	20.93	4.46	YES	66.67	4.46	YES	28.00	4.46	YES
Interactions:									
Time x Temp	3.44	3.84	NO	2.13	3.84	NO	2.00	3.84	NO
Time x pH	0.79	3.84	NO	2.67	3.84	NO	0.00	3.84	NO
Temp x pH	2.87	3.84	NO	1.33	3.84	NO	1.00	3.84	NO

The results of Table 6 indicate that the temperature and pH have a significant effect on the rate of solids separation for all three solids separation techniques. Of the various main effects and interactions evaluated, the pH had the most significant effect on solids separation rates. The effect of time, on the other hand, was not significant. The results of Table 6 also indicate that there were no significant two-way interactions between the factors of time, temperature, and pH.

Since the time was not a significant variable in these tests, results obtained at different times can be averaged to give a more precise indication of the effects of temperature and pH. The results for settling, filtration, and centrifugation are shown in Figures 14, 15, and 16, respectively. In these three figures, each data point represents the average of three tests at the three different digestion times for the indicated pH and temperature. The experimental error for these data is indicated by the standard deviation bar which was calculated in accordance with standard statistical procedures by taking the square root of the mean square of the time x temperature x pH interaction.

As shown in Figure 14, the settling rate increased (30-min sludge volume decreased) with digestion temperature, and at the highest temperature, appeared to go through a maximum (minimum) at pH 2.5. However, the absolute rate of settling was low. At the optimum conditions, the sludge settled to only about 87% of its initial volume in 30 minutes.

The filtration rate (shown in Figure 15) also increased with digestion temperature, and at all temperatures, the maximum filtration rate occurred at a pH of 2.5.

The centrifugation rate (Figure 16) also increased (10-min sludge volume decreased) with digestion temperature, and the best centrifugation rates were again obtained in the vicinity of pH 2.5.

Based on the settling, filtration, and centrifugation results, the optimum treatment conditions appear to be pH 2.5 and 95°C. Since time was not a significant variable over the range investigated, the minimum time of 10 minutes would be selected as the optimum digestion time.

Fitchburg Waste Activated Sludge--

Similar tests were conducted for Fitchburg WAS (4.0% solids), and results of the solid-liquid separation tests are presented in Table 7.

The results of the analysis of variance for the solid-liquid separation data are given in Table 8. For filtration the results indicate that pH is the only significant variable. For settling all three variables (time, temperature, and pH) and all three interactions (time x temperature, time x pH, and temperature x pH) are significant. For centrifugation, all three variables and one interaction (time x temperature) are significant.

For settling, in which all three variables and interactions are significant, Figure 17 gives the volume of sludge remaining after 30 minutes settling time (calculated as a percentage of the initial 900 ml volume of sludge) as a function of pH for various digestion times and temperatures.

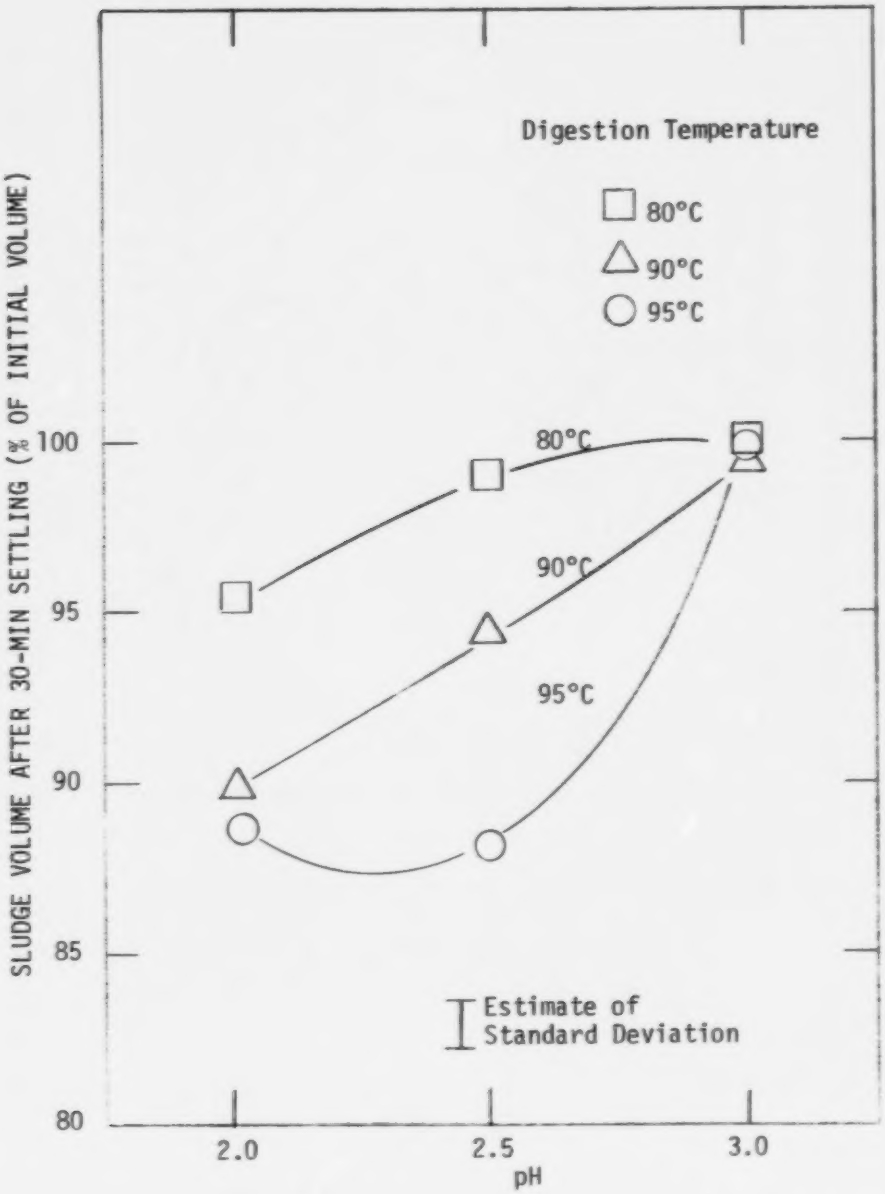

Figure 14. Effect of treatment conditions on settling rate for Brockton WAS.

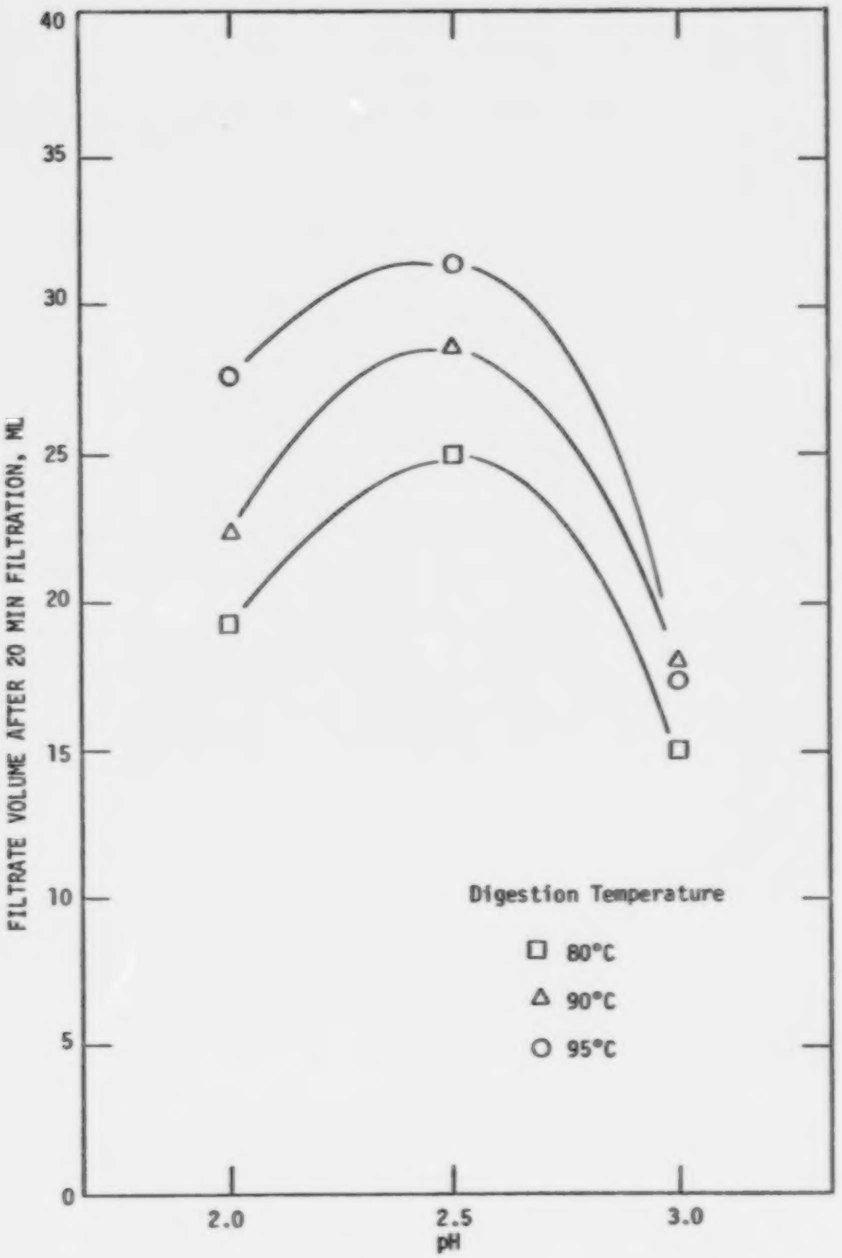

Figure 15. Effect of treatment conditions on filtration rate for Brockton WAS.

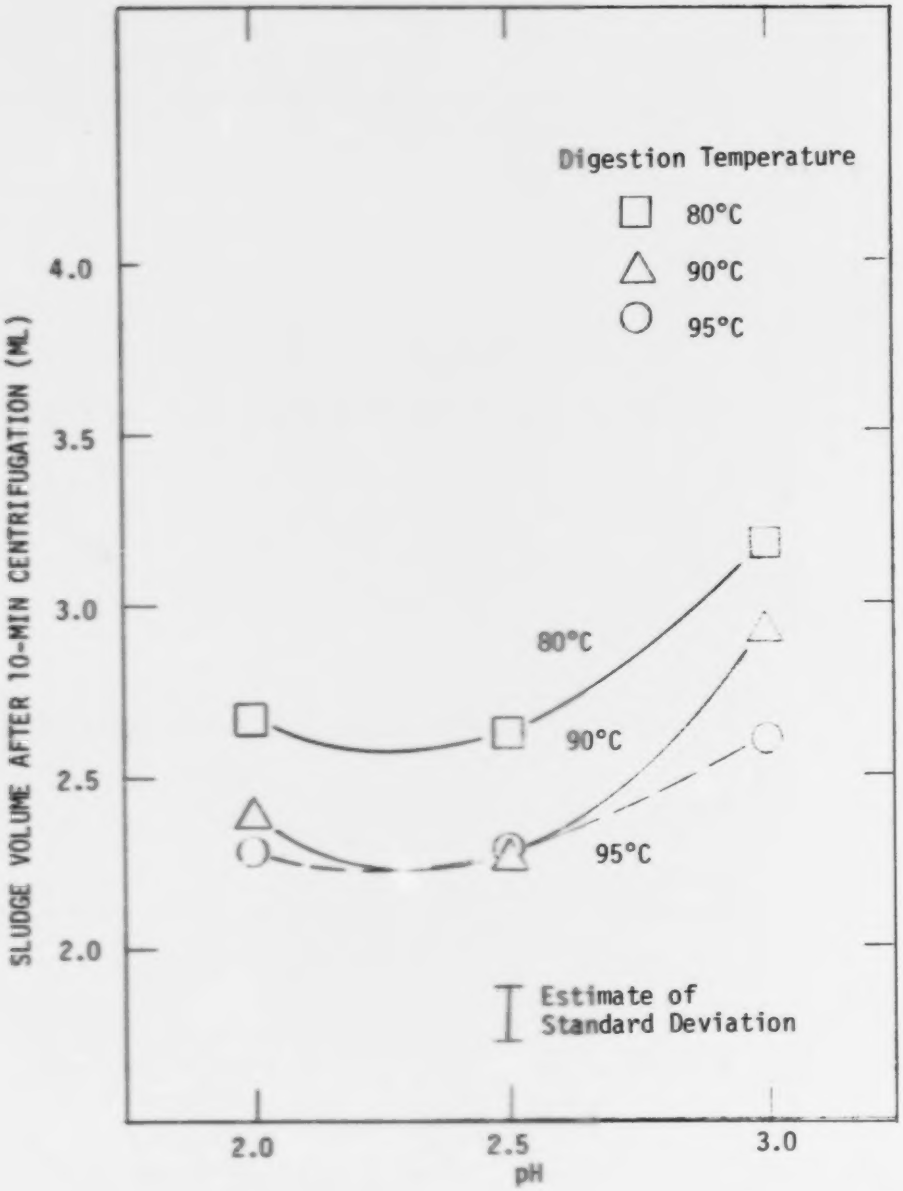

Figure 16. Effect of treatment conditions on centrifugation rate for Brockton WAS.

TABLE 7. EFFECT OF TREATMENT CONDITIONS ON SOLID-LIQUID SEPARATION RATES FOR FITCHBURG WAS

TREATMENT CONDITIONS			SOLIDS SEPARATION RATE		
Time (min.)	Temp. (°C)	pH	Settling 30-min sludge vol., %	Filtration 20-min filtrate vol., ml	Centrifugation 10-min sludge vol., ml
10	80	2.0	93.3	28	2.0
		2.5	94.4	34	1.8
		3.0	97.8	21	2.0
	90	2.0	94.4	30	2.4
		2.5	94.4	30	2.0
		3.0	95.6	18	2.1
	95	2.0	91.1	22	1.8
		2.5	90.0	32	1.6
		3.0	93.3	22	1.8
30	80	2.0	96.7	30	1.8
		2.5	95.6	28	1.8
		3.0	97.8	18	2.0
	90	2.0	92.2	36	1.8
		2.5	92.2	37	1.8
		3.0	93.9	24	1.8
	95	2.0	88.9	30	1.8
		2.5	88.9	32	1.7
		3.0	93.3	18	1.8
60	80	2.0	94.4	22	2.1
		2.5	91.1	33	1.9
		3.0	97.2	18	2.1
	90	2.0	86.7	32	1.7
		2.5	84.4	36	1.6
		3.0	87.8	26	1.7
	95	2.0	86.7	40	1.5
		2.5	85.6	40	1.5
		3.0	88.9	28	1.6

TABLE 8. ANALYSIS OF VARIANCE RESULTS FOR SOLIDS SEPARATION TESTS (FITCHBURG WASTE ACTIVATED SLUDGE)

Source of variation	Settling			Filtration			Centrifugation		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?
Time	184.205	4.46	YES	1.844	4.46	NO	23.539	4.46	YES
Temperature	257.436	4.46	YES	4.285	4.46	NO	43.934	4.46	YES
pH	78.359	4.46	YES	19.343	4.46	YES	13.400	4.46	YES
Interactions:									
Time x Temp	38.256	3.84	YES	1.978	3.84	NO	22.449	3.84	YES
Time x pH	7.487	3.84	YES	0.506	3.84	NO	3.070	3.84	NO
Temp x pH	4.769	3.84	YES	0.353	3.84	NO	1.749	3.84	NO

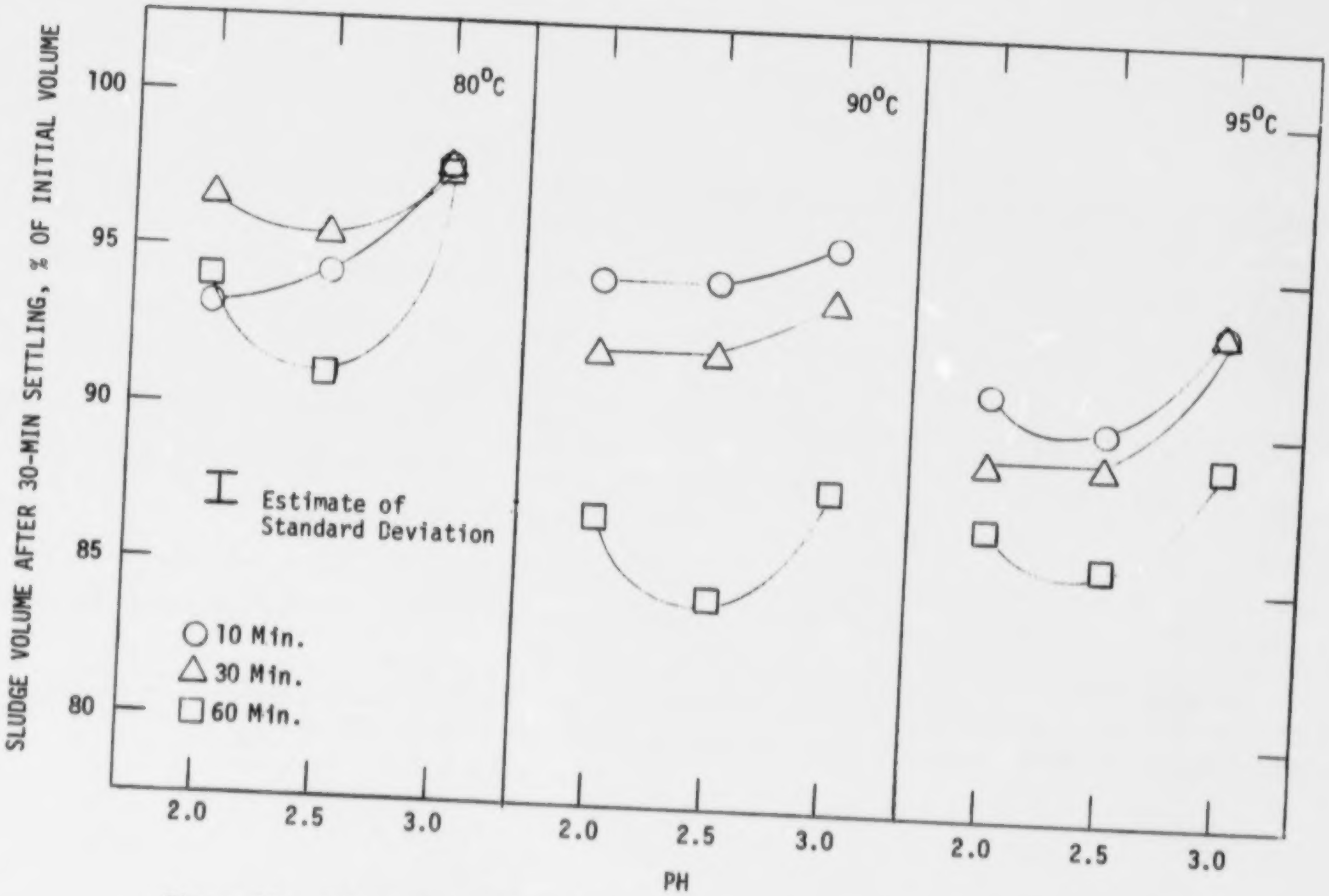

Figure 17. Effect of treatment conditions on settling rate for Fitchburg WAS.

In examining Figure 17 for the optimum treatment conditions with respect to settling, it can be seen that the point at pH 2.5/90°C/60 minutes gave the minimum interface height after 30 minutes. The next lowest point is at pH 2.5/95°C/60 minutes, so that the optimum conditions for settling appear to be pH 2.5/90-95°C/60 minutes.

For filtration, only one variable --pH-- was significant. The filtration results (volume of filtrate collected after 20 minutes from an initial volume of 45 ml) is shown in Figure 18. Each of the points shown in Figure 18 was determined by averaging the filtrate volume over time and temperature at each pH (average of nine points). The optimum filtration rate occurs at a pH of 2.5.

For centrifugation, all three variables (time, temperature, and pH) were significant, as well as the time x temperature interaction. The centrifugation results (sludge volume remaining after 10 minutes of centrifugation from an initial volume of 10 ml) are shown in Figure 19 as a function of pH for various times and temperatures. From these data it appears that the optimum conditions for centrifugation are pH 2.5/95°C/60 minutes.

Based on the above solid-liquid separation tests the preferred treatment conditions for Fitchburg WAS are a pH of 2.5, a temperature of 95°C, and a digestion time of 60 minutes.

Brockton Primary Plus Waste Activated Sludge--

A 50:50 mixture of Brockton primary and WAS containing 4.5% total solids was tested using the same full-factorial experimental design as for the secondary sludges. Results for the solid-liquid separation rates as a function of treatment conditions are given in Table 9.

The analysis of variance for the solid-liquid separation data is given in Table 10. For settling, all three of the factors (time, temperature, and pH) are significant and one interaction (time x temperature) is significant. However, the time factor and the interaction are only marginally significant since the Test F is close to the $F_{0.95}$. For filtration, only the pH has a significant influence on the rate, and for centrifugation, only pH and temperature have a significant effect on the solid-liquid separation rate.

Results for settling at various treatment conditions are shown in Figure 20. In general the settling rate passed through a maximum at pH 2.5, and at this pH, the most rapid settling occurred for a digestion time of 10 minutes and a temperature of 90 or 95°C. The digestion time had an inconsistent effect on settling rate giving rise to the significant time x temperature interaction: at 80°C a digestion time of 60 minutes gave the best settling rate while at 95°C it gave the worst settling rate.

For filtration, only pH was significant, and at each pH the data for different times and temperatures were averaged (9 tests at each pH) and plotted in Figure 21. The filtration rate passes through a maximum at a pH of 2.5.

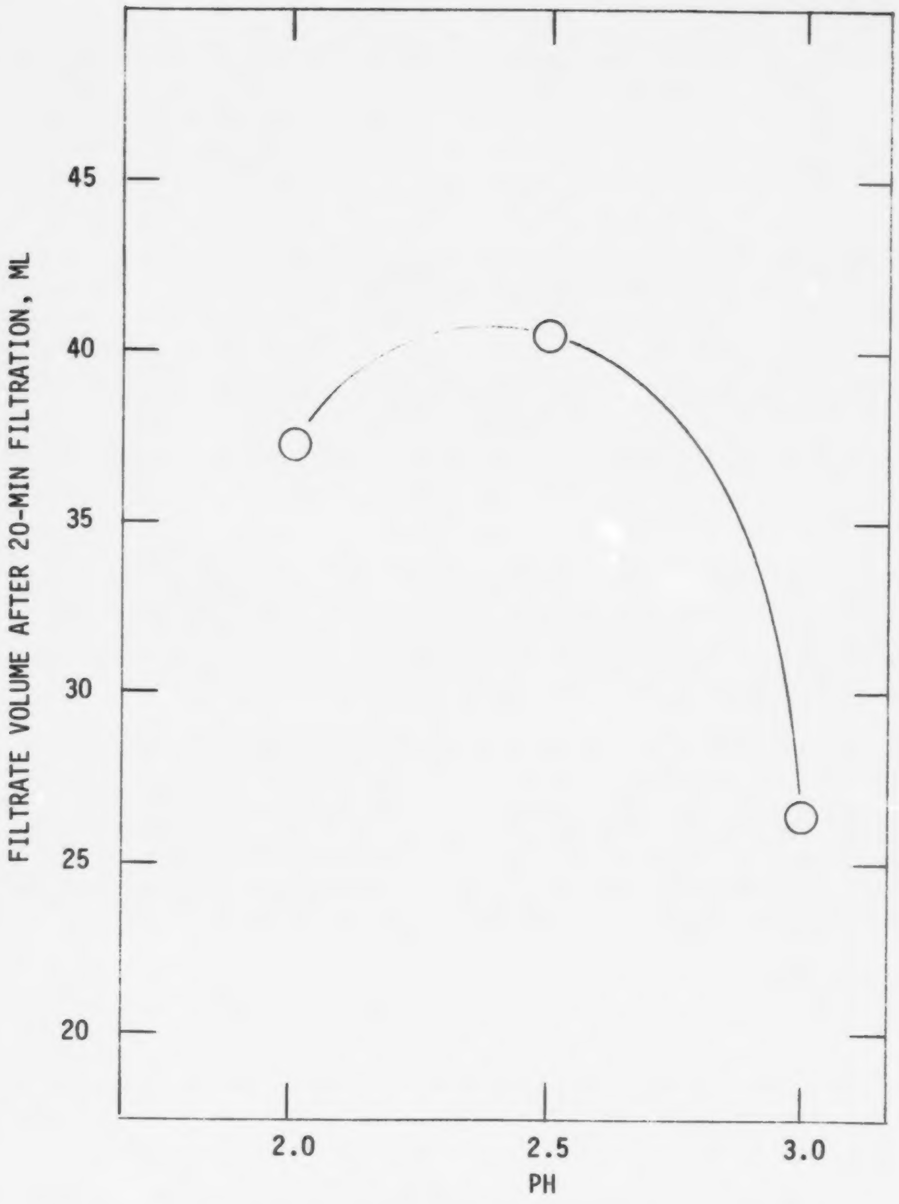

Figure 18. Effect of treatment conditions on filtration rate for Fitchburg WAS.

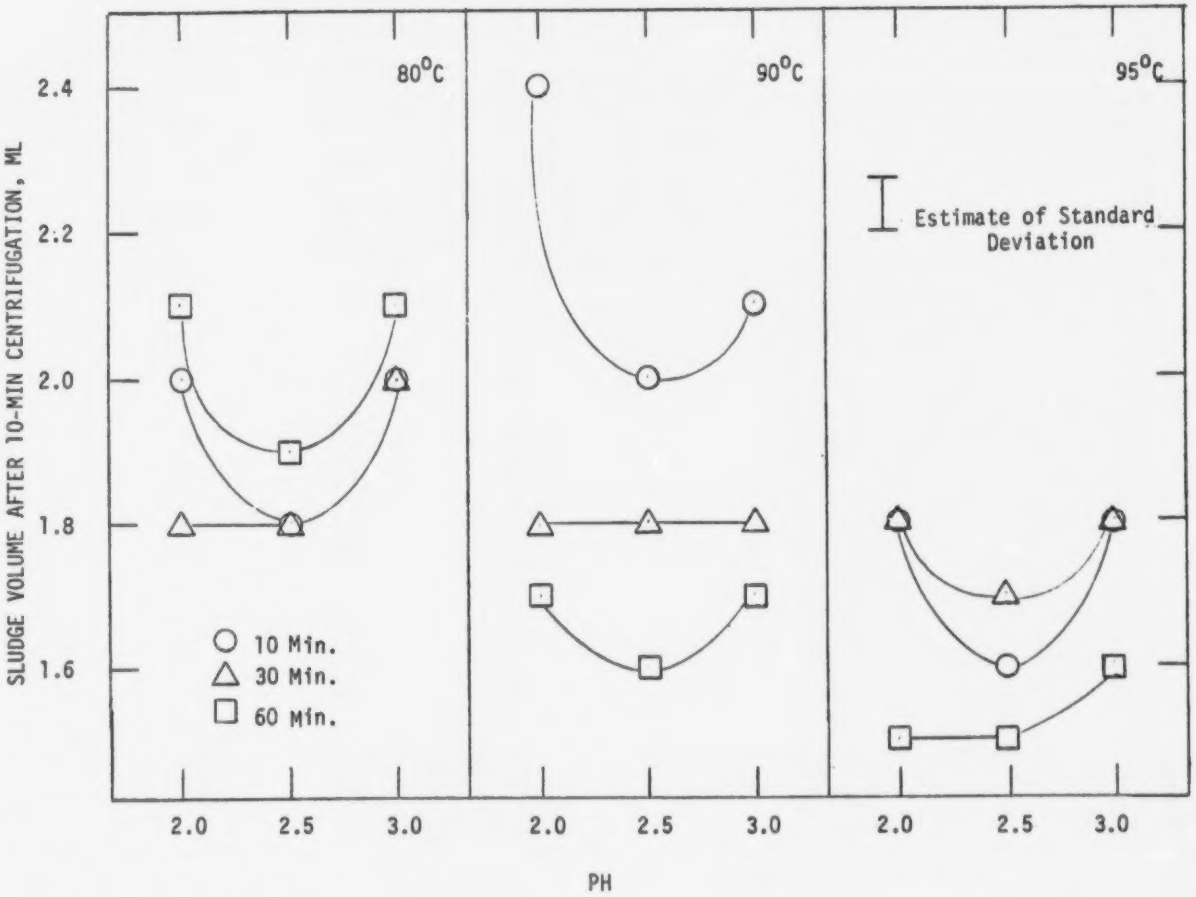

Figure 19. Effect of treatment conditions on centrifugation rate for Fitchburg WAS.

TABLE 9. EFFECT OF TREATMENT CONDITIONS ON SOLID-LIQUID SEPARATION RATES FOR BROCKTON PRIMARY PLUS WAS

TREATMENT CONDITIONS			SOLIDS SEPARATION RATE		
Time (min.)	Temp. (°C)	pH	Settling 30-min sludge vol., %	Filtration 20-min filtrate vol., ml	Centrifugation 10-min sludge vol., ml
10	80	2.0	98.3	38	2.4
		2.5	97.2	38	2.4
		3.0	98.9	24	3.8
	90	2.0	96.1	38	2.2
		2.5	94.4	40	2.2
		3.0	98.3	17	2.7
	95	2.0	95.6	34	2.3
		2.5	94.4	38	2.4
		3.0	97.8	22	3.0
30	80	2.0	97.8	34	2.4
		2.5	98.3	39	2.6
		3.0	99.4	22	2.6
	90	2.0	97.8	37	2.2
		2.5	96.7	39	2.2
		3.0	98.9	27	2.5
	95	2.0	97.8	40	2.3
		2.5	95.0	41	2.3
		3.0	98.3	22	2.5
60	80	2.0	97.8	32	2.4
		2.5	96.7	36	2.4
		3.0	97.8	26	2.6
	90	2.0	93.3	38	2.3
		2.5	94.4	39	2.4
		3.0	97.8	22	2.6
	95	2.0	97.8	38	2.3
		2.5	96.7	40	2.2
		3.0	99.4	29	2.5

TABLE 10. ANALYSIS OF VARIANCE RESULTS FOR SOLIDS SEPARATION TESTS (BROCKTON PRIMARY PLUS WAS)

Source of variation	Settling			Filtration			Centrifugation		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?
Time	4.544	4.46	YES	0.602	4.46	NO	3.152	4.46	NO
Temperature	9.809	4.46	YES	0.789	4.46	NO	4.541	4.46	YES
pH	24.069	4.46	YES	78.583	4.46	YES	15.380	4.46	YES
Interactions:									
Time x temp	5.264	3.84	YES	1.183	3.84	NO	1.202	3.84	NO
Time x pH	0.548	3.84	NO	0.884	3.84	NO	3.788	3.84	NO
Temp x pH	2.006	3.84	NO	0.645	3.84	NO	0.441	3.84	NO

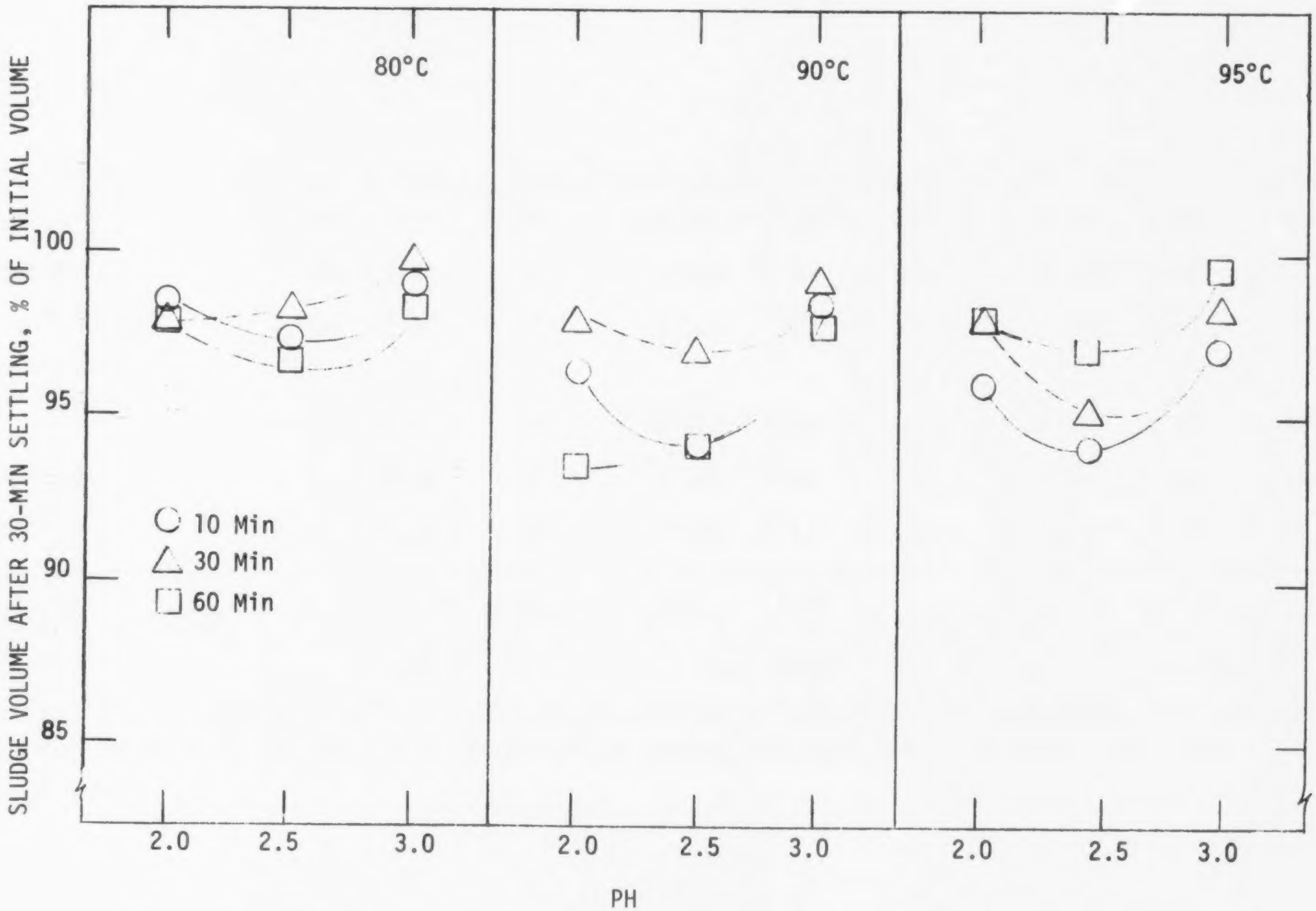

Figure 20. Effect of treatment conditions on settling rate for Brockton primary plus WAS.

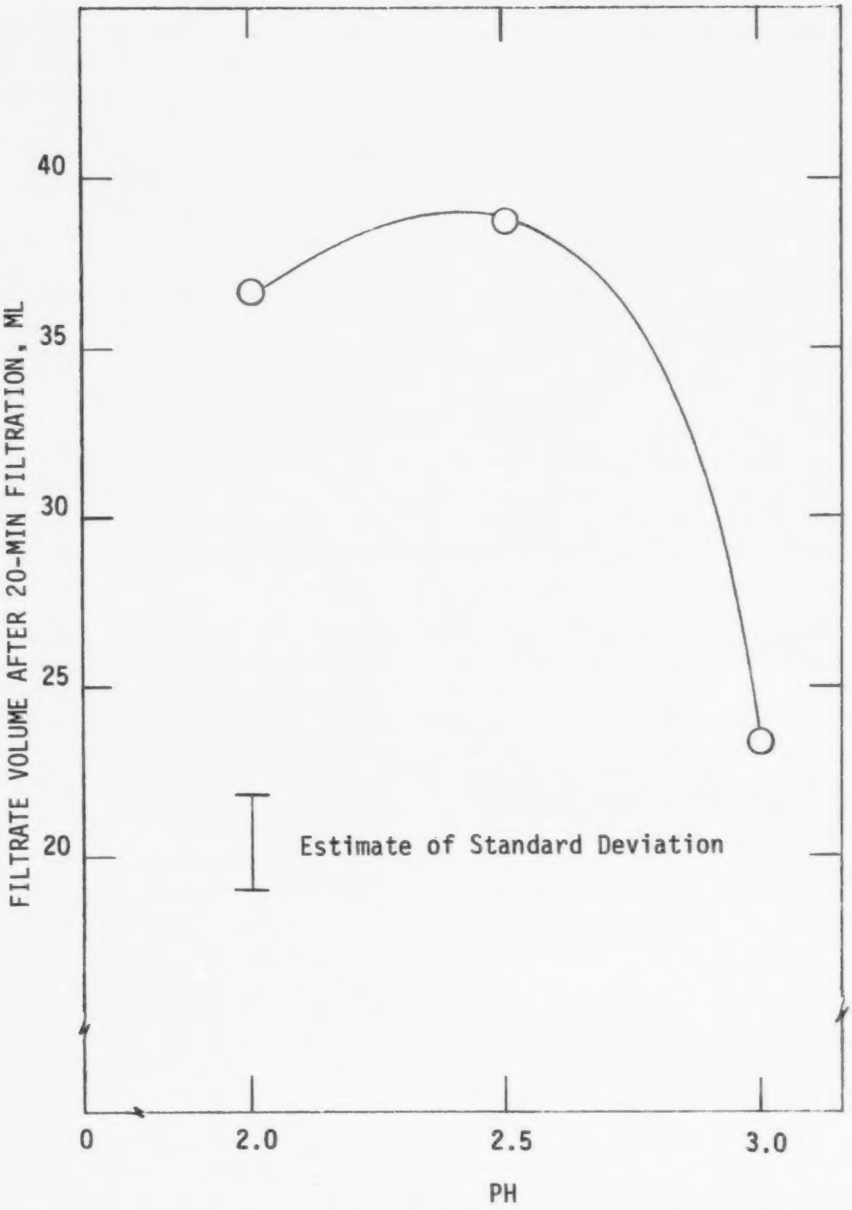

Figure 21. Effect of treatment conditions on filtration rate for Brockton primary plus WAS.

Figure 22 gives the results for centrifugation as a function of the significant variables (pH and temperature). Results at pH 2.0 and 2.5 are essentially identical. The centrifugation rate appears to pass through a maximum at 90°C, but the results at 90 and 95°C are nearly the same. In fact, considering the magnitude of the standard deviation, there is little difference between the three temperatures. This is consistent with the results of the analysis of variance (Table 10) which indicated that temperature is only a "marginally significant" variable at the 95% confidence level.

Fitchburg Primary Plus Waste Activated Sludge--

Similar tests were conducted with a 50:50 mixture of Fitchburg primary and WAS. As shown in Table 3, the mean total solids concentration of this sludge was 4.22% with a rather large standard deviation of 1.18%. The 95% confidence interval on the mean is from 3.3% to 5.1% total solids. The problem of obtaining a representative sample of sludge was particularly evident during these tests. The primary sludge contained some rather large clumps and the distribution of clumps between samples could not be controlled. The centrifugation results were particularly erratic, probably because of the small sample size. The sludge centrifuged quite rapidly reaching its maximum compaction within 30 seconds. However the volume of sludge remaining after maximum compaction was reached was much more dependent on the distribution of solid "clumps" between centrifuge tubes than on the hot-acid treatment conditions to which the samples were subjected. After reviewing the data it was decided that the centrifugation results were not amenable to a detailed analysis.

Table 11 gives the results for settling and filtration as a function of treatment conditions, and the analysis of variance results are given in Table 12. For filtration, no variables or interactions were found to be significant. This could be the result of uncontrolled solids distribution when the treated samples are poured into the filters. Since the filtrate volume was only 45 ml, these tests could be subject to the same type of errors as the centrifugation tests.

For settling, a large volume was used and could have resulted in a more homogeneous distribution of suspended solids between samples. The results of the analysis of variance indicate that pH and time are significant factors and the time-temperature interaction is also significant. However, the time and time-temperature interactions are only marginally significant at the 95% confidence level, and considering the problems encountered in obtaining reproducible results with this sludge, the use of a higher confidence level for testing significance may be justified. In this case, only the pH would be significant.

Figure 23 gives the settling rate for Fitchburg primary plus WAS as a function of pH. Each point indicates the average of nine tests conducted at various times and temperatures at the indicated pH. The rate of settling is greatest following treatment of this sludge at pH 2.5.

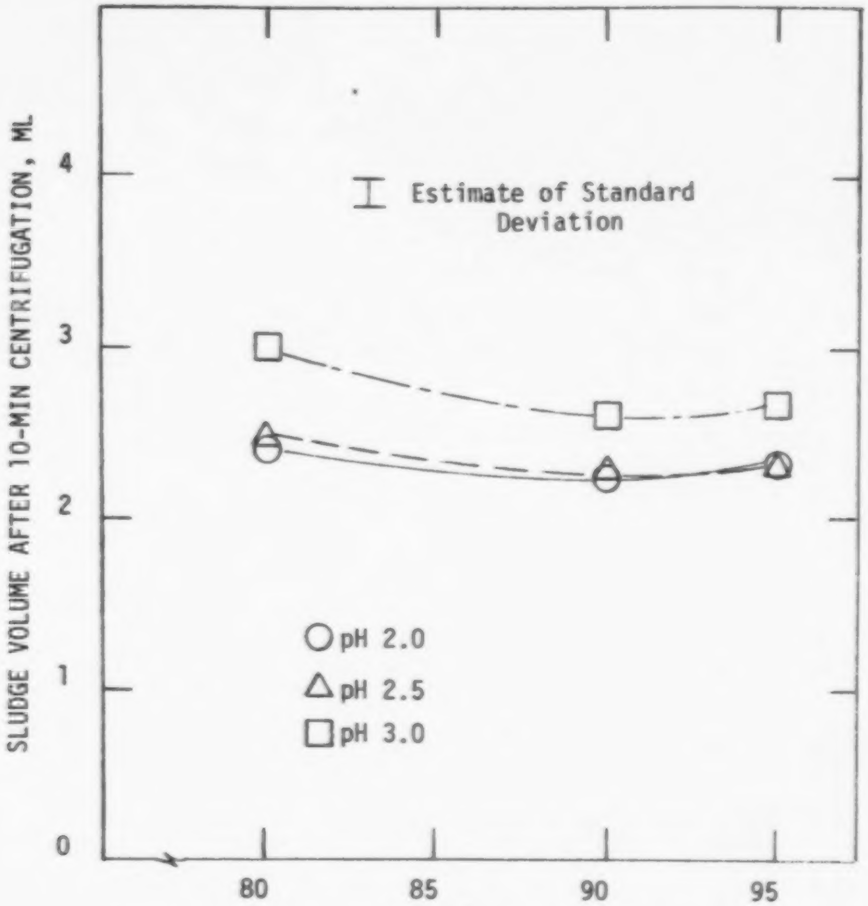

Figure 22. Effect of treatment conditions on centrifugation rate for Brockton primary plus WAS.

TABLE 11. EFFECT OF TREATMENT CONDITIONS ON SOLID-LIQUID SEPARATION RATE FOR FITCHBURG PRIMARY PLUS WAS

TREATMENT CONDITIONS			SOLIDS SEPARATION RATE	
Time (min)	Temp (^{o}C)	pH	Settling 30-min sludge vol, %	Filtration 20-min filtrate vol, ml
10	80	2.0	83.3	22
		2.5	75.6	38
		3.0	80.0	42
	90	2.0	85.6	32
		2.5	74.4	38
		3.0	83.3	25
	95	2.0	77.8	38
		2.5	68.9	44
		3.0	82.2	33
30	80	2.0	88.3	27
		2.5	81.1	36
		3.0	83.3	39
	90	2.0	77.8	40
		2.5	74.4	34
		3.0	81.1	33
	95	2.0	82.2	38
		2.5	83.3	39
		3.0	87.2	29
60	80	2.0	83.3	38
		2.5	72.2	38
		3.0	77.8	33
	90	2.0	79.4	28
		2.5	76.7	34
		3.0	89.4	26
	95	2.0	75.6	40
		2.5	74.4	40
		3.0	76.7	41

TABLE 12. ANALYSIS OF VARIANCE RESULTS FOR SOLIDS SEPARATION TESTS (FITCHBURG PRIMARY PLUS WAS)

Source of variation	Settling			Filtration		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?
Time	4.512	4.46	YES	0.030	4.46	NO
Temperature	1.156	4.46	NO	2.721	4.46	NO
pH	15.500	4.46	YES	2.030	4.46	NO
Interactions:						
Time x temp	5.433	3.84	YES	0.981	3.84	NO
Time x pH	1.195	3.84	NO	0.551	3.84	NO
Temp x pH	2.536	3.84	NO	1.742	3.84	NO

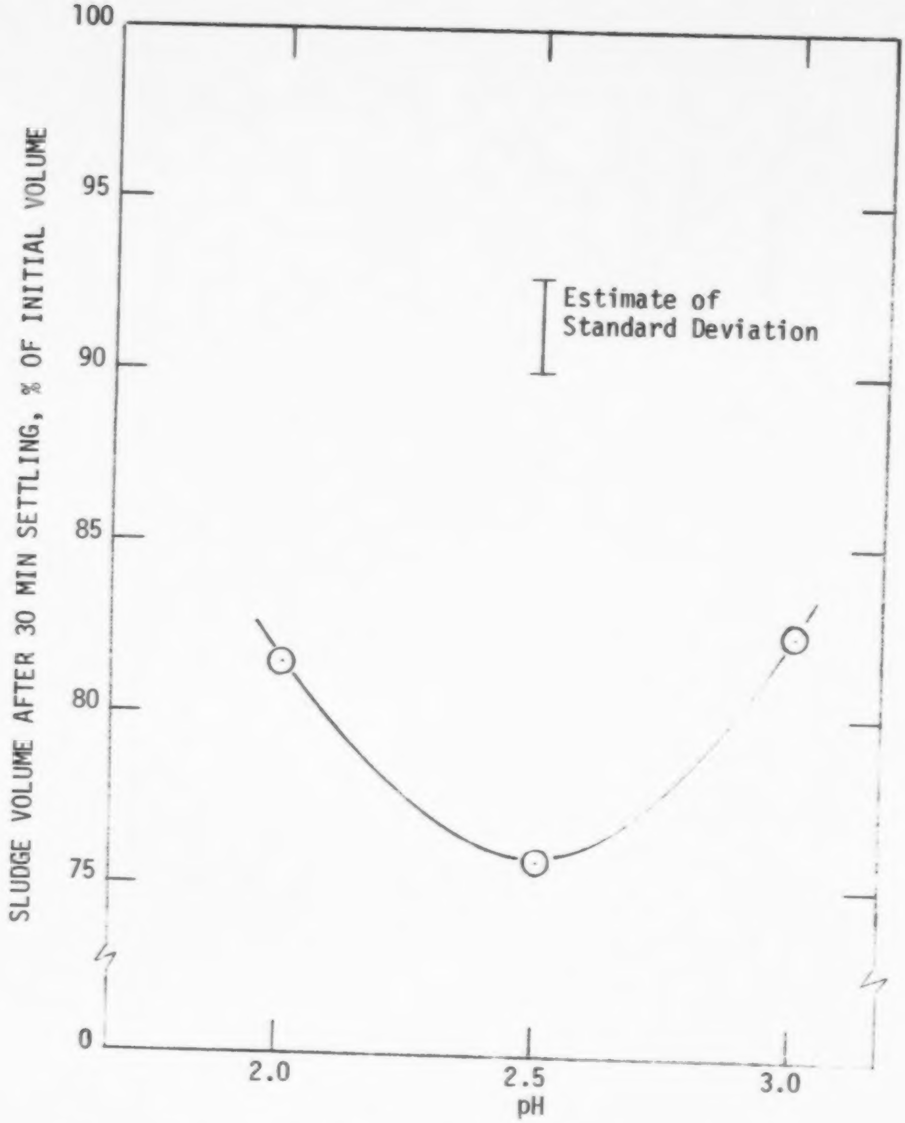

Figure 23. Effect of treatment conditions on settling rate for Fitchburg primary plus WAS.

Solubilization of Sludge Constituents

One of the important aspects of the hot acid process is the extent to which it solubilizes various constituents of the sludge. Using the sampling, analysis, and data reduction procedures described above (Methods and Materials), the degree of solubilization was determined for suspended solids, suspended COD, and suspended metals. More detailed and better controlled experiments to specifically evaluate the solubilization of heavy metal were subsequently conducted, and results from these tests are presented and discussed in Section 6.

Effect of Process Variables on Degree of Solubilization--

In order to determine the effect of the major process variables on the degree of solubilization of various sludge constituents, samples were obtained and analyzed during the full-factorial experiments described above. Samples were analyzed for total solids, COD, zinc, and copper. Because of the large number of tests, analyses were not performed for other metals during the full-factorial experiments. Zinc and copper were selected for analysis in order to indicate the range of expected heavy-metals solubilization: zinc is relatively difficult to solubilize. The results of these tests confirm the difficulty of copper solubilization: under all conditions covered by the full-factorial experiment, there was virtually no solubilization of copper. Therefore only the zinc results are presented below for these tests. While cadmium would have been a more interesting metal than copper to follow, the cadmium concentrations in some samples of the sludges was judged to be too close to the detection limit (0.2 mg/l) to give meaningful results in all cases.

Brockton Waste Activated Sludge--The solubilization results for Brockton WAS are shown as a function of treatment conditions in Table 13. All of the sludge samples listed in Table 13 were obtained from the same batch of Brockton waste activated sludge. With each set of three tests, a sample of raw sludge (indicated in Table 13 by "no treatment") was analyzed. The mean concentrations and standard deviations for the nine raw sludge samples are given below.

Assay	Mean Concentration	Standard Deviation
Total Solids (mg/l)	42,100	5,100
Dissolved Solids (mg/l)	1,500	490
Total COD (mg/l)	53,600	5,440
Dissolved COD (mg/l)	2,790	1,550
Total Zinc (mg/l)	60	14
Dissolved Zinc (mg/l)	0.39	0.26

The largest standard deviations (relative to the mean) were obtained for dissolved solids, dissolved COD and dissolved zinc. If the samples are placed in chronological order according to Table 4, there is a general increase in the dissolved constituents with sludge age. For example the dissolved COD of the fresh sludge was 325 mg/l, but after 4 days of refrigerated storage it had increased to 4,480 mg/l. Because of the low

TABLE 13. EFFECT OF TREATMENT CONDITIONS ON SOLUBILICATION OF SLUDGE CONSTITUENTS FOR BROCKTON WAS

Treatment conditions			Concentrations in wet sludge (mg/ℓ)						Degree of solubilization (%)		
Time (min.)	Temperature (°C)	pH	Solids*		COD		Zinc		Suspended Solids	Suspended COD	Suspended Zinc
			Tot.	Dis.	Tot.	Dis.	Tot.	Dis.			
10	80	2.0	41,400	6,800	48,000	2,650	58	37	2.2	4.9	63.8
		2.5	42,000	5,100	55,400	2,380	58	19	5.6	3.7	32.7
		3.0	43,600	9,900	56,600	2,540	59	7.6	18.8	3.9	12.9
--- No treatment ---			39,900	665	50,800	325	45	0.28	----	----	----
	90	2.0	41,100	14.400	50,600	7,890	58	42	23.2	7.6	71.9
		2.5	32,600	8,040	49,400	6,440	48	8	10.0	4.5	14.9
		3.0	41,900	7,580	48,300	5,900	39	2	10.4	3.4	2.6
--- No treatment ---			37,450	2,030	50,200	4,400	38	1	----	----	----
	95	2.0	43,200	9,560	50,200	6,980	69	14	8.2	6.4	19.7
		2.5	46,600	9,040	52,500	6,090	64	6	9.0	4.3	6.7
		3.0	49,700	7,900	52,500	5,510	64	1	9.0	3.1	0.8
--- No treatment ---			42,725	2,190	54,400	4,010	68	0.5	----	----	----
30	80	2.0	44,400	8,620	55,800	5,310	68	35	7.2	5.3	51.3
		2.5	48,400	8,620	56,800	4,750	78	20	8.7	4.2	25.4
		3.0	48,400	6,290	56,000	4,440	81	3.8	6.7	3.7	4.4
--- No treatment ---			48,825	1,690	51,800	2,480	67	0.26	----	----	----
	90	2.0	35,600	9,260	30,600	6,550	52	46	14.5	17.7	88.5
		2.5	43,650	6,630	43,400	4,070	48	14	8.5	6.4	29.2
		3.0	42,500	6,170	58,900	3,780	56	4.1	9.5	4.2	7.3
--- No treatment ---			41,600	950	54,600	1,370	58	0.14	----	----	----
	95	2.0	38,600	9,660	27,400	6,990	33	19	11.4	11.0	56.9
		2.5	35,800	8,880	35,900	6,840	31	12	12.9	7.5	37.7
		3.0	39,700	7,660	47,500	5,790	40	1	12.4	3.0	1.3
--- No treatment ---			38,575	1,585	47,100	4,480	62	0.5	----	----	----
60	80	2.0	43,400	11,260	39,400	6,360	49	19	14.5	8.3	38.3
		2.5	41,000	8,150	45,200	5,670	55	10	9.3	5.5	17.6
		3.0	42,800	7,270	52,500	5,320	67	2	10.6	4.0	2.4
--- No treatment ---			34,975	1,475	52,000	3,370	52	0.4	----	----	----
	90	2.0	49,200	10,460	52,100	5,720	66	32	10.6	4.6	48.3
		2.5	41,900	8,620	53,300	5,600	74	13	10.2	4.3	17.3
		3.0	49,800	7,480	62,500	6,230	81	6.6	8.7	4.7	7.9
--- No treatment ---			50,000	1,720	66,400	3,470	86	0.23	----	----	----
	95	2.0	42,000	10,140	55,800	6,670	62	36	13.2	9.5	57.9
		2.5	42,800	8,180	51,500	4,750	57	18	11.4	6.4	31.3
		3.0	42,600	6,260	58,500	4,340	60	5.5	9.3	4.9	8.8
--- No treatment ---			45,175	1,295	55,600	1,540	60	0.21	----	----	----

* Includes sulfate solids added with H_2SO_4.

concentrations of dissolved zinc, it is likely that experimental errors in the analysis also added to the scatter of the data. These changes in dissolved concentrations with time were assumed to have no effect on the ease of solubilization of suspended material, and, if an effect did occur, the randomization of the tests was designed to preclude misinterpretation of aging effects for the effects of the primary variables being investigated.

In order to determine the factors which have a significant influence on the degree of solubilization, an analysis of variance was performed on the solubilization data of Table 13. The results are given in Table 14. For suspended solids, none of the factors investigated had a significant influence on the degree of solubilization within the ranges investigated. Furthermore, none of the interactions between factors were significant. Therefore all 27 data points were averaged to give a mean percent solids solubilized. The mean solubilization and 95% confidence interval are:

Percent Solids Solubilized = 10.6% ± 1.6%

For COD, the results of Table 14 indicate that, of the factors and interactions evaluated, only the pH has a significant effect on the degree of solubilization. Thus the results at different times and temperatures can be averaged to give the percent COD solubilized at each pH. The mean percent solubilization (average of 9 tests at each pH) as a function of pH is:

pH	Mean Percent COD Solubilized	95% Confidence Interval
3.0	3.9	± 0.5
2.5	5.2	± 1.0
2.0	8.0	± 3.7

It is apparent from these data that the percent solubilization of COD increases as the pH decreases.

Results for zinc solutilization are also shown in Table 14. As was the case for COD solubilization, the pH is the only factor which influences the degree of zinc solubilization. The analysis of variance also indicates a significant interaction between time and temperature. However, neither the main effect for time nor the main effect for temperature is significant, and the Test-F for the interaction is only slightly greater than $F_{0.95}$. Therefore, the interaction was neglected, and the mean percent solubilization of zinc (average of 9 tests at each pH) as a function of pH is:

pH	Mean Percent Zinc Solubilized	95% Confidence Interval
3.0	5.4	± 3.1
2.5	23.9	± 7.4
2.0	55.2	±15.1

As for COD, the degree of zinc solubilization increases with decreasing pH.

TABLE 14. ANALYSIS OF VARIANCE RESULTS FOR SOLUBILIZATION TESTS (BROCKTON WAS)

Source of variation	Suspended solids			COD			Zinc		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?
Time	0.053	4.46	NO	2.87	4.46	NO	2.49	4.46	NO
Temperature	0.66	4.46	NO	0.95	4.46	NO	1.49	4.46	NO
pH	0.51	4.46	NO	7.28	4.46	YES	71.67	4.46	YES
Interactions:									
Time x temp.	0.96	3.84	NO	1.66	3.84	NO	4.79	3.84	YES
Time x pH	0.39	3.84	NO	1.37	3.84	NO	1.09	3.84	NO
Temp x pH	1.24	3.84	NO	0.43	3.84	NO	2.58	3.84	NO

Fitchburg Waste Activated Sludge--Table 15 gives the analytical and solubilization results as a function of treatment condition for Fitchburg WAS. The average concentration and standard deviation for the nine raw sludge samples are given below.

Assay	Mean Concentration	Standard Deviation
Total Solids (mg/l)	39,600	1,600
Dissolved Solids (mg/l)	2,240	250
Total COD (mg/l)	41,600	2,600
Dissolved COD (mg/l)	4,910	930
Total Zinc (mg/l)	25	3
Dissolved Zinc (mg/l)	0.7	0.2

Compared to the Brockton WAS, this sludge exhibited much less change in dissolved solids concentrations with storage time as evidenced by the much smaller standard deviations (relative to their respective means) for the dissolved constituents.

Table 16 gives the results of the analysis of variance for the Fitchburg WAS. For suspended solids, none of the factors investigated appeared to have a significant effect on solubilization within the ranges investigated. However, the interaction between temperature and time was determined to be significant. The temperature-time interaction is shown in Figure 24 where the percent suspended solids solubilization is plotted against temperature for various digestion times. Each data point represents the mean of the results obtained at the three different pH levels. The fact that the curves are not parallel indicates an interaction between temperature and time, and the analysis of variance indicates that this interaction is statistically significant. The interaction appears to indicate that the degree of solubilization is relatively low either at low temperature and low digestion times or at high temperature and high digestion times. This result is unexpected. The significance of the interaction depends largely on the high solubilities obtained during the set of three tests conducted at 80°C and 60 minutes. Further tests should be conducted to reproduce this result before concluding that it is real.

The mean solubilization and 95% confidence interval for the Fitchburg WAS are:

Percent Solids Solubilized = 10.1% ± 1.8%

This value is in very good agreement with the corresponding value (10.6%) determined for the Brockton WAS.

For COD, the results of Table 16 indicate that all of the factors investigated had a significant effect on the degree of solubilization and that the interaction between temperature and pH was significant. Figure 25 shows the percent COD solubilization as a function of pH for various times

TABLE 15. EFFECT OF TREATMENT CONDITIONS ON SOLUBILIZATION OF SLUDGE CONSTITUENTS FOR FITCHBURG WAS

Treatment conditions			Concentration in wet sludge (mg/ℓ)						Solubilization (%)		
Time (min)	Temp (°C)	pH	Solids* Tot.	Solids* Dis.	COD Tot.	COD Dis.	Zinc Tot.	Zinc Dis.	Sus. solids	Sus. COD	Sus. zinc
10	80	2.0	38,700	7,510	28,700	5,170	32	27	1.5	5.7	84.0
		2.5	35,600	7,740	31,600	4,600	25	14	8.5	3.0	54.5
		3.0	39,000	6,040	31,500	4,830	22	9	4.6	3.9	38.9
-- No treatment --			38,800	1,872	39,900	3,760	26	0.8	----	----	----
	90	2.0	44,100	10,270	45,400	7,950	26	17	8.9	4.9	64.7
		2.5	43,600	8,570	46,300	7,260	27	15	7.0	3.1	54.7
		3.0	43,400	8,320	46,700	7,100	26	14	10.5	2.7	52.9
-- No treatment --			41,400	2,480	43,300	6,010	26	0.5	----	----	----
	95	2.0	46,400	13,560	54,800	9,740	23	19	17.2	8.5	82.1
		2.5	45,900	10,520	45,600	8,150	22	18	11.9	6.5	81.2
		3.0	41,600	9,000	46,600	6,810	19	10	12.9	3.0	50.8
-- No treatment --			42,100	2,270	44,400	5,560	20	0.7	----	----	----
30	80	2.0	39,600	8,740	41,600	6,040	30	19	7.6	3.5	62.1
		2.5	37,900	6,420	40,900	5,520	30	14	3.8	2.1	44.8
		3.0	39,100	6,340	43,700	6,150	30	8	7.7	3.6	24.1
-- No treatment --			40,100	1,890	41,300	4,760	30	1	----	----	----
	90	2.0	40,800	8,800	38,800	5,630	28	16	7.1	5.5	56.0
		2.5	39,337	8,090	40,700	4,980	30	15	8.2	3.5	52.4
		3.0	36,900	7,050	37,300	5,020	27	11	9.9	4.0	37.7
-- No treatment --			37,900	2,040	37,600	3,690	25	(13)	----	----	----
	95	2.0	44,600	12,020	46,600	9,450	27	18	14.1	8.6	66.0
		2.5	41,300	10,250	50,300	8,680	27	13	12.9	6.1	47.2
		3.0	41,000	8,670	42,800	7,510	25	8	12.8	4.2	30.6
-- No treatment --			37,200	2,200	43,400	5,960	25	0.5	----	----	----
60	80	2.0	45,400	16,770	47,900	8,540	20	19	25.7	7.1	94.9
		2.5	38,100	10,070	36,400	7,390	19	15	13.1	6.0	78.4
		3.0	42,300	9,090	42,400	6,980	22	14	13.0	3.9	62.8
-- No treatment --			38,800	2,400	44,400	5,550	21	0.5	----	----	----
	90	2.0	43,000	9,730	31,200	7,130	22	18	8.1	8.2	81.3
		2.5	39,900	8,210	28,600	6,460	22	13	7.2	6.2	57.9
		3.0	40,700	7,140	27,800	5,900	18	7	8.1	4.0	36.8
-- No treatment --			40,500	2,480	42,500	4,990	24	0.6	----	----	----
	95	2.0	37,500	10,480	27,400	7,150	28	18	11.9	13.6	63.0
		2.5	36,500	8,310	24,700	5,820	27	14	8.2	9.0	50.0
		3.0	32,700	7,260	27,000	5,510	24	8	10.6	6.8	30.4
-- No treatment --			39,800	2,510	38,000	3,950	26	1	----	----	----

* Treated samples include sulfate solids added as H_2SO_4.

( ) Indicates questionable value. Average value for other untreated samples was used in calculating percent solubilized.

TABLE 16. ANALYSIS OF VARIANCE RESULTS FOR SOLUBILIZATION TESTS (FITCHBURG WAS)

Source of variation	Suspended solids			COD			Zinc		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?
Time	1.55	4.46	NO	46.91	4.46	YES	12.68	4.46	YES
Temperature	3.49	4.46	NO	56.97	4.46	YES	1.45	4.46	NO
pH	1.06	4.46	NO	57.38	4.46	YES	40.98	4.46	YES
Interactions:									
Time x temp	5.52	3.84	YES	3.49	3.84	NO	7.54	3.84	YES
Time x pH	0.75	3.84	NO	3.73	3.84	NO	0.20	3.84	NO
Temp x pH	0.40	3.84	NO	7.39	3.84	YES	0.89	3.84	NO

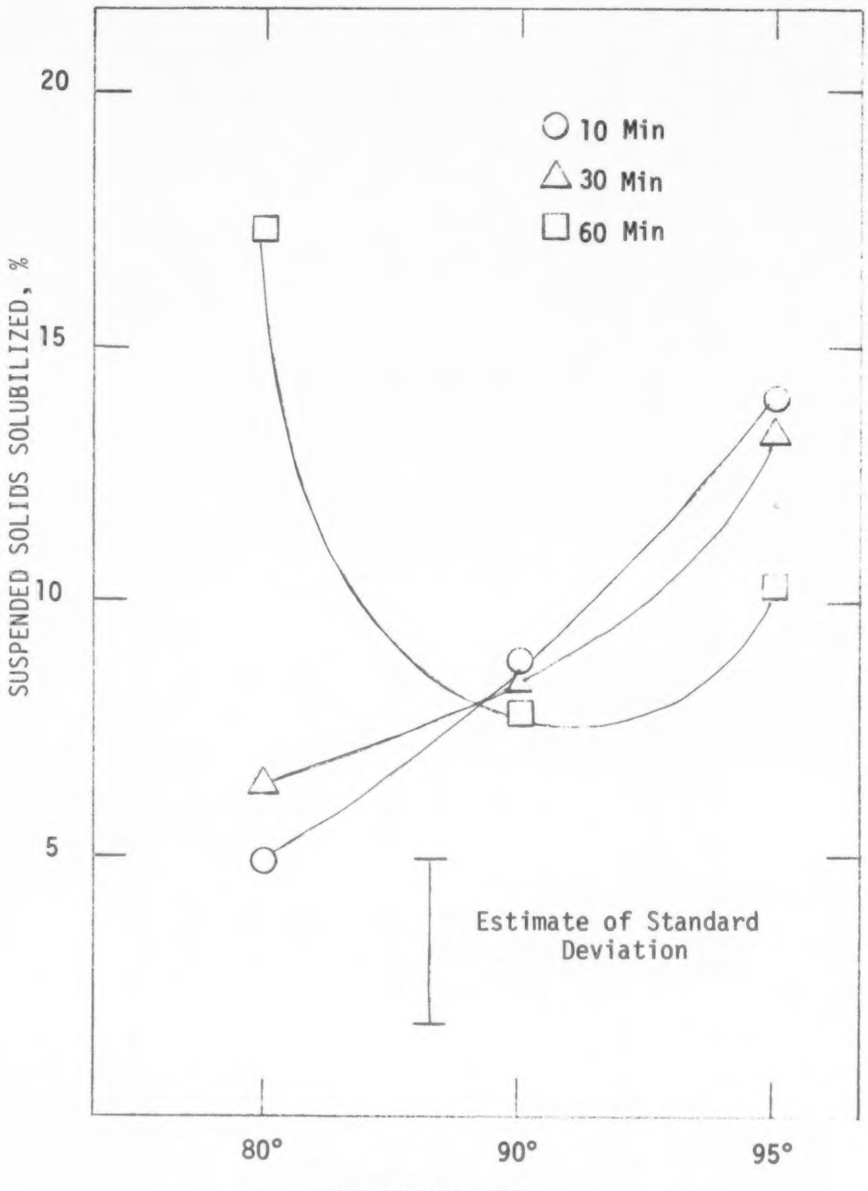

Figure 24. The effect of time and temperature on the degree of suspended solids solubilization for Fitchburg WAS.

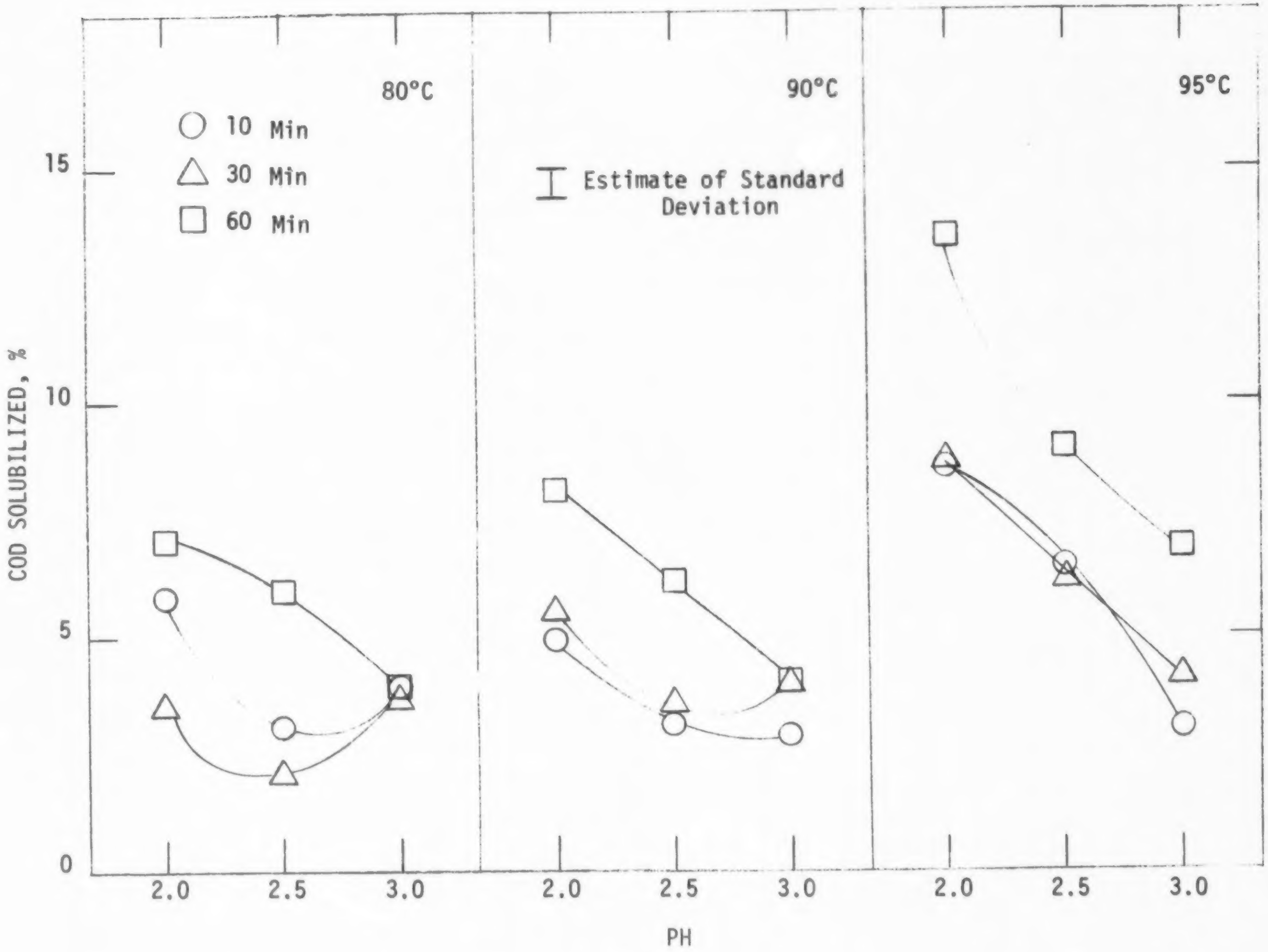

Figure 25. Effect of treatment conditions on the degree of COD solubilization for Fitchburg WAS.

and temperatures. In general the degree of COD solubilization increased with increasing time and temperature and increased with decreasing pH. The degree of solubilization ranged from 2% at 30 minutes, 80°C, and pH 2.5 to 13.7% at 60 minutes, 95°C, and pH 2.0.

The analysis of variance results for zinc solubilization, also shown in Table 16, indicate that pH, and time are significant variables and the time-temperature interaction is also significant. Figure 26 illustrates the dependence of zinc solubilization on pH and time. Each point is the average of the results at the three temperature levels for the indicated time and pH. The degree of solubilization increased linearly with decreasing pH and reached a level of about 80% solubilization at pH 2.0. The data appear to indicate lower solubilization at 30 minutes digestion time than at either 10 or 60 minutes digestion time.

Brockton Primary Plus Waste Activated Sludge--Solubilization results for the 50:50 mixture of Brockton primary and WAS are shown in Table 17. The average concentrations and standard deviations for the nine raw sludge samples are given below.

Assay	Mean Concentration	Standard Deviation
Total Solids (mg/l)	45,300	4,200
Dissolved Solids (mg/l)	1,290	330
Total COD (mg/l)	54,500	3,320
Dissolved COD (mg/l)	2,590	940
Total Zinc (mg/l)	78	7
Dissolved Zinc (mg/l)	0.2	0.05

The ratio of the standard deviation to the mean gives a measure of the relative degree of scatter about the mean. As noted for the other sludge samples, the scatter of results is noticably greater for dissolved species (ratios of 0.25 to 0.36) than for total species (ratios of 0.06 to 0.09). The greater standard deviations for dissolved constituents can be attributed to significant changes in dissolved concentrations with sludge age. However the changes were less than for the Brockton WAS discussed above.

Results of the analysis of variance for the Brockton primary plus WAS mixture are shown in Table 18. Within the ranges investigated, none of the variables or interactions had a significant effect on solubilization of suspended solids. The mean percent solubilization (average of 27 data points) and 95% confidence interval are:

Percent Suspended Solids Solubilized = 6.2% ± 1.1%

Thus the degree of suspended solids solubilization is significantly less for the primary-WAS mixture than for unmixed WAS (10.6%).

As indicated in Table 18, all three variables (time, temperature, and pH) and time-temperature interaction had a significant effect on the degree of COD solubilization. Figure 27 shows the percent COD solubilized as a

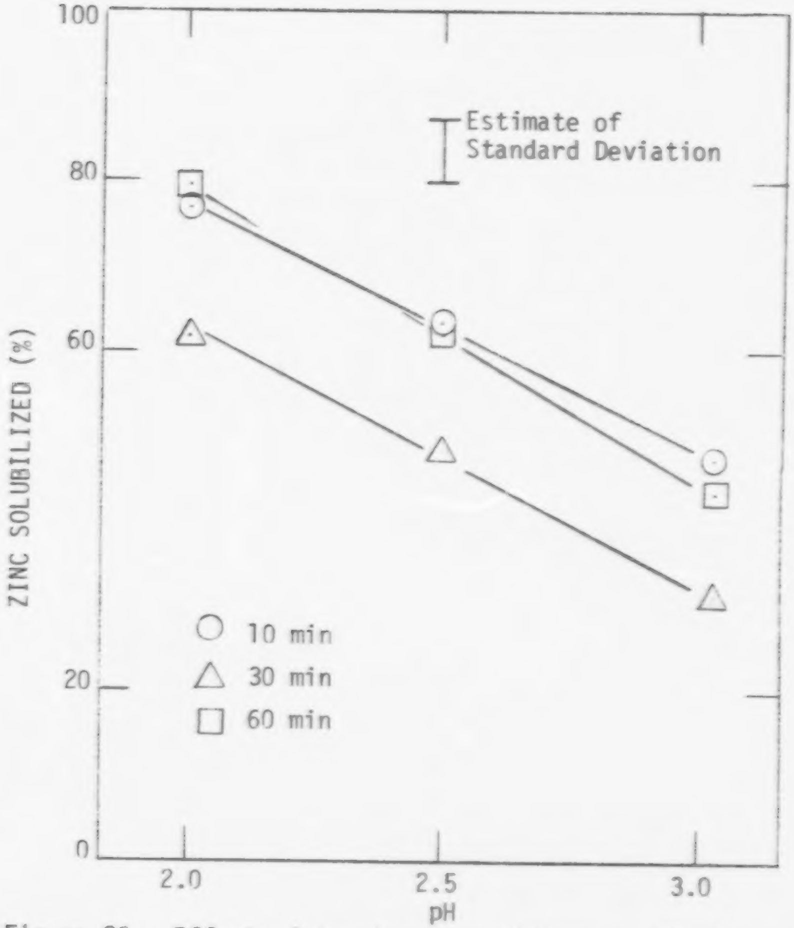

Figure 26. Effect of treatment conditions on the degree of zinc solubilization for Fitchburg WAS.

TABLE 17. EFFECT OF TREATMENT CONDITIONS ON SOLUBILIZATION OF SLUDGE CONSTITUENTS FOR BROCKTON PRIMARY PLUS WAS

Treatment conditions			Concentrations in wet sludge (mg/ℓ)						Solubilization (%)		
Time (min)	Temp (°C)	pH	Solids*		COD		Zinc		Sus. solids	Sus. COD	Sus. zinc
			Tot.	Dis.	Tot.	Dis.	Tot.	Dis.			
10	80	2.0	50,300	7,750	51,400	3,200	70	27	6.0	4.8	38.5
		2.5	50,300	7,326	53,700	1,640	72	20	7.2	1.6	27.7
		3.0	43,400	4,170	55,600	2,480	73	0.8	4.6	3.1	1.0
-- No treatment --			43,200	711	53,100	800	74	0.1	----	----	----
	90	2.0	44,300	8,580	55,400	5,290	77	14	6.6	4.3	17.9
		2.5	43,200	6,800	54,200	4,130	76	1.1	4.7	2.1	1.1
		3.0	54,600	5,220	51,800	4,570	83	0.6	3.8	3.1	0.4
-- No treatment --			53,200	1,740	51,000	3,060	79	0.3	----	----	----
	95	2.0	50,400	9,300	57,700	5,830	84	9	8.2	5.2	10.5
		2.5	52,000	7,140	57,500	4,850	86	0.8	5.4	3.4	0.7
		3.0	50,900	5,280	59,400	4,750	90	0.2	5.0	3.1	0.0
-- No treatment --			41,100	1,330	61,400	3,000	72	0.2	----	----	----
30	80	2.0	43,900	8,820	60,500	4,680	82	14	8.5	2.1	16.9
		2.5	46,800	6,360	55,500	3,760	86	0.5	4.3	0.6	0.3
		3.0	41,400	5,410	53,400	4,340	88	0.3	6.7	1.7	0.1
-- No treatment --			44,600	1,260	52,900	3,470	89	0.2	----	----	---
	90	2.0	44,800	10,410	53,700	4,710	70	.16	13.1	5.9	22.6
		2.5	47,900	8,190	54,300	4,010	73	6	8.8	4.5	8.0
		3.0	50,900	4,930	59,700	3,540	84	0.3	4.8	3.3	0.1
-- No treatment --			51,200	1,100	57,500	1,640	71	0.2	----	----	----
	95	2.0	43,300	6,550	63,700	4,940	71	0.2	2.4	2.5	0.0
		2.5	41,500	6,980	51,800	5,020	75	0.7	6.4	3.3	0.7
		3.0	42,400	5,060	51,400	5,180	71	0.4	5.4	3.6	0.3
-- No treatment --			46,100	1,360	53,200	3,430	71	0.2	----	----	----
60	80	2.0	43,800	7,960	59,400	5,270	82	13	5.0	3.7	15.6
		2.5	41,500	5,080	56,500	4,330	90	0.6	0.1	2.2	0.4
		3.0	42,300	4,190	56,700	4,540	79	0.3	2.2	2.5	0.1
-- No treatment --			41,700	1,770	56,700	3,180	89	0.2	----	----	----
	90	2.0	46,400	9,060	56,900	5,680	85	7	7.5	5.0	8.0
		2.5	44,800	6,960	55,900	4,590	82	0.5	6.1	3.0	0.4
		3.0	40,500	5,680	54,200	4,500	88	0.2	7.7	3.0	0.0
-- No treatment --			42,800	1,220	52,300	2,990	79	0.2	----	----	----
	95	2.0	50,200	10,530	59,000	6,550	90	22	11.8	8.3	24.3
		2.5	54,500	8,860	62,500	5,550	95	7	9.0	5.3	7.2
		3.0	40,900	5,320	47,100	4,100	84	0.2	7.0	5.1	0.0
-- No treatment --			44,000	1,090	52,700	1,780	77	0.2	----	----	----

* Treated samples include sulfate solids added as H_2SO_4.

TABLE 18. ANALYSIS OF VARIANCE RESULTS FOR SOLUBILIZATION TESTS (BROCKTON PRIMARY PLUS WAS)

Source of variance	Suspended solids			COD			Zinc		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?	TestF	$F_{0.95}$	Signif.?
Time	0.350	4.46	NO	5.103	4.46	YES	1.487	4.46	NO
Temperature	1.778	4.46	NO	13.795	4.46	YES	1,861	4.46	NO
pH	2.338	4.46	NO	12,455	4.46	YES	13.099	4.46	YES
Interactions:									
Time x temp	3.148	3.84	NO	6.567	3.84	YES	3.152	3.84	NO
Time x pH	0.156	3.84	NO	1.242	3.84	NO	0.361	3.84	NO
Temp x pH	0.281	3.84	NO	0.528	3.84	NO	0.541	3.84	NO

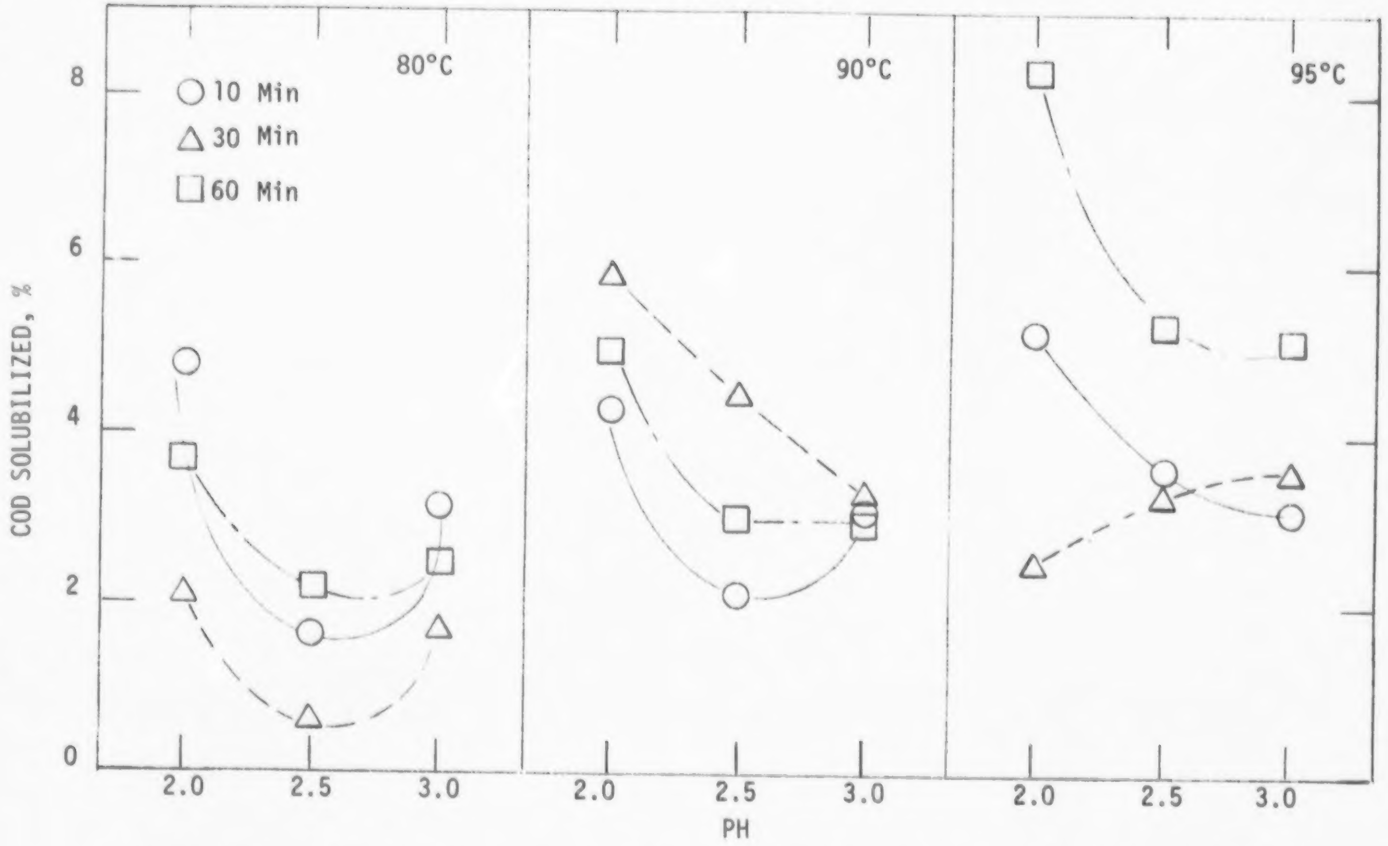

Figure 27. Effect of treatment conditions on the degree of COD solubilization for Brockton primary plus WAS.

function of pH for different digestion times and temperatures. These data do not indicate a consistent monotonic variation of COD solubilization with any of the three factors investigated, and the significance of all the factors plus one interaction may be attributable to the small estimated error calculated for this set of tests. It would be advisable to repeat the analysis of variance using the two-way interactions in addition to the three-way interaction to estimate the experimental error before testing the significance of the main factors.

For zinc, only the pH was observed to have a significant effect on solubilization. Therefore the results obtained at each pH for the nine different time and temperature combinations were averaged to give the following mean solubilization and 95% confidence intervals.

pH	Mean Percent Zinc Solubilized	95% Confidence Interval
3.0	0.2	± 0.25
2.5	5.2	± 6.9
2.0	17.1	± 8.4

The 95% confidence intervals are quite large, reflecting the large range over which the degree of solubilization varied at each pH. For example, the degree of solubilization at pH 2.0 ranged from zero to 38.5 percent. It is noteworthy that the degree of zinc solubilization was substantially less than for the unmixed Brockton WAS (which gave 55% solubilized at pH 2.0).

Fitchburg Primary Plus Waste Activated Sludge--Solubilization results for the 50:50 mixture of Fitchburg primary and WAS are shown in Table 19. The average concentrations and standard deviations for the nine raw sludge samples are:

Assay	Mean Concentration	Standard Deviation
Total Solids (mg/l)	42,200	11,800
Dissolved Solids (mg/l)	2,030	620
Total COD (mg/l)	36,400	11,000
Dissolved COD (mg/l)	2,920	710
Total Zinc (mg/l)	24	7
Dissolved Zinc (mg/l)	1	0.5

With the exception of dissolved zinc, the standard deviation relative to the mean is approximately the same for the total and dissolved constituents (ratios from 0.24 to 0.30). The scatter in results for dissolved constituents can be attributed to changed during storage. The scatter in results for total constituents can be attributed largely to sampling inaccuracies resulting from the presence of relatively large clumps of solids in this sludge sample. These sampling errors can occur each time a portion of a sample of sludge is transferred from one container to another.

The results of the analysis of variance for the Fitchburg primary plus secondary sludge mixture are given in Table 20. For suspended solids, none of the factors or interactions had a significant effect on the degree of

TABLE 19. EFFECT OF TREATMENT CONDITIONS ON SOLUBILIZATION OF SLUDGE CONSTITUENTS FOR FITCHBURG PRIMARY PLUS WAS

Treatment conditions			Concentrations in wet sludge (mg/ℓ)						Solubilization (%)		
Time	Temp.		Solids*		COD		Zinc		Sus.	Sus.	Sus.
(min)	(°C)	pH	Tot.	Dis.	Tot.	Dis.	Tot.	Dis.	solids	COD	zinc
10	80	2.0	31,200	12,170	42,500	3,450	25	18	24.6	3.5	70.8
		2.5	16,500	6,320	42,000	2,880	20	12	12.1	2.1	57.9
		3.0	31,500	5,220	43,600	2,740	20	10	7.1	1.7	52.6
-- No treatment --			50,400	1,470	39,200	2,040	26	1	----	----	----
	90	2.0	30,500	6,680	31,300	4,690	22	12	1.6	3.3	52.4
		2.5	39,900	6,820	22,100	4,390	15	10	4.0	3.4	64.3
		3.0	34,900	4,120	24,800	4,640	15	2	1.8	4.1	7.1
-- No treatment --			50,700	2,170	52,900	3,770	34	1	----	----	----
	95	2.0	33,900	7,380	39,700	4,250	18	12	5.3	2.8	62.3
		2.5	35,400	5,860	33,200	3,850	21	9	2.7	2.0	36.8
		3.0	34,300	3,480	52,200	4,450	21	2	1.1	2.5	0.0
-- No treatment --			49,300	1,760	43,600	3,240	25	2	----	----	----
30	80	2.0	40,600	6,360	51,800	3,980	29	11	1.2	2.3	36.4
		2.5	43,200	6,160	40,700	3,500	21	12	2.8	1.7	55.7
		3.0	21,200	3,400	25,300	3,140	15	2	3.9	1.3	9.1
-- No treatment --			50,200	1,820	37,100	2,840	27	0.7	----	----	----
	90	2.0	43,600	20,600	29,200	2,900	18	13	39.4	3.5	71.4
		2.5	21,100	10,830	24,400	2,720	17	12	37.9	3.4	69.7
		3.0	26,500	3,680	26,400	2,540	16	6	4.4	2.4	35.5
-- No treatment --			28,900	1,270	36,400	1,960	20	0.5	----	----	----
	95	2.0	41,800	8,040	35,200	5,480	28	19	4.7	4.8	66.9
		2.5	50,600	6,890	30,000	5,280	22	12	3.1	5.0	52.8
		3.0	24,800	5,890	30,900	5,120	19	3	10.8	4.2	12.1
-- No treatment --			52,200	2,220	45,800	3,990	34	0.8	----	----	----
60	80	2.0	28,700	7,520	26,300	3,900	20	15	0.1	4.2	73.7
		2.5	24,500	8,010	20,500	3,860	20	14	7.7	5.4	68.4
		3.0	19,700	4,380	26,700	3,110	13	5	0.0	0.8	33.3
-- No treatment --			32,600	3,360	31,800	2,910	23	1	----	----	----
	90	2.0	15,900	6,620	22,500	3,700	19	11	0.9	2.7	53.5
		2.5	14,400	6,700	21,700	3,770	15	7	11.7	3.2	9.1
		3.0	20,200	4,740	33,400	3,790	15	2	5.8	2.0	1.5
-- No treatment --			20,300	2,410	21,700	3,180	14	1.8	----	----	----
	95	2.0	41,900	9,090	51,200	4,380	24	16	8.9	4.1	65.4
		2.5	28,300	6,470	38,000	4,060	20	14	6.2	4.8	65.6
		3.0	38,000	5,040	29,000	3,000	14	4	5.5	2.5	23.7
-- No treatment --			45,100	1,760	18,800	2,360	15	0.9	----	----	----

* Treated samples include sulfate solids added as H_2SO_4.

TABLE 20. ANALYSIS OF VARIANCE RESULTS FOR SOLUBILIZATION TESTS (FITCHBURG PRIMARY PLUS WAS)

Source of variance	Suspended solids			COD			Zinc		
	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?	Test F	$F_{0.95}$	Signif.?
Time	1.460	4.46	NO	1.627	4.46	NO	0.034	4.46	NO
Temperature	1.387	4.46	NO	7.671	4.46	YES	1.382	4.46	NO
pH	1.035	4.46	NO	10.018	4.46	YES	23.169	4.46	YES
Interactions:									
Time x temp	3.637	3.84	NO	9.024	3.84	YES	5.117	3.84	YES
Time x pH	0.342	3.84	NO	5.014	3.84	YES	0.323	3.84	NO
Temp x pH	0.607	3.84	NO	1.899	3.84	NO	0.612	3.84	NO

solubilization. The mean solubilization for suspended solids (average of 27 data points) and 95% confidence interval are:

Percent Suspended Solids Solubilized = 8.0% ± 4%

The large confidence interval reflects the wide range of values obtained and implies a higher level of experimental error associated with the tests on this sludge.

For COD solubilization, temperature, pH, and both the time-temperature and the time-pH interactions were significant. Figure 28 shows the percent COD solubilized as a function of pH for various digestion times. The degree of COD solubilization was about the same for both pH 2.0 and 2.5, while pH 3.0 gave relatively low COD solubilizations. In general, COD solubilization increased with increasing temperature. However, with the exception of pH 3 and 80°C, the mean degree of COD solubilization was between 3 and 4% for all conditions tested. Thus, the selection of conditions does not appear to have a dramatic influence on COD solubilization.

For zinc solubilization, pH was the only significant variable, and the time-temperature interactions was the only significant interaction. The results at each pH (nine tests) were averaged to give the mean solubilization and 95% confidence intervals shown below.

pH	Mean Percent Zinc Solubilized	95% Confidence Interval
3.0	19%	± 14%
2.5	53%	± 15%
2.0	61%	± 9%

The degree of zinc solubilization for this sludge sample is approximately the same as for the sample of Fitchburg WAS at pH 2.0 and 2.5 and is significantly greater than for the primary-WAS mixture of Brockton sludge.

Summary of Metals Solubilizations at Various pH's--

In addition to the matrix of tests described above, metals solubilizations were determined for various other tests. Most of these other tests were conducted with Brockton waste activated sludge. As shown in Table 14, pH is the only factor that is significant at the 95% confidence level for solubilization of zinc bound by this sludge. Therefore the results of all the tests can be presented as a function of pH only. Table 21 summarizes the metals solubilization results for Brockton WAS. These results include the full factorial experiments described above, averaged over time and temperature at the indicated pH.

Of the various metals assayed, zinc was the easiest to solubilize, chrome and lead were more difficult to solubilize, and the solubilization of cadmium was highly variable. In general the degree of solubilization increased with decreasing pH, but the range of solubilization at each pH was quite broad. The variability of results, particularly for cadmium led

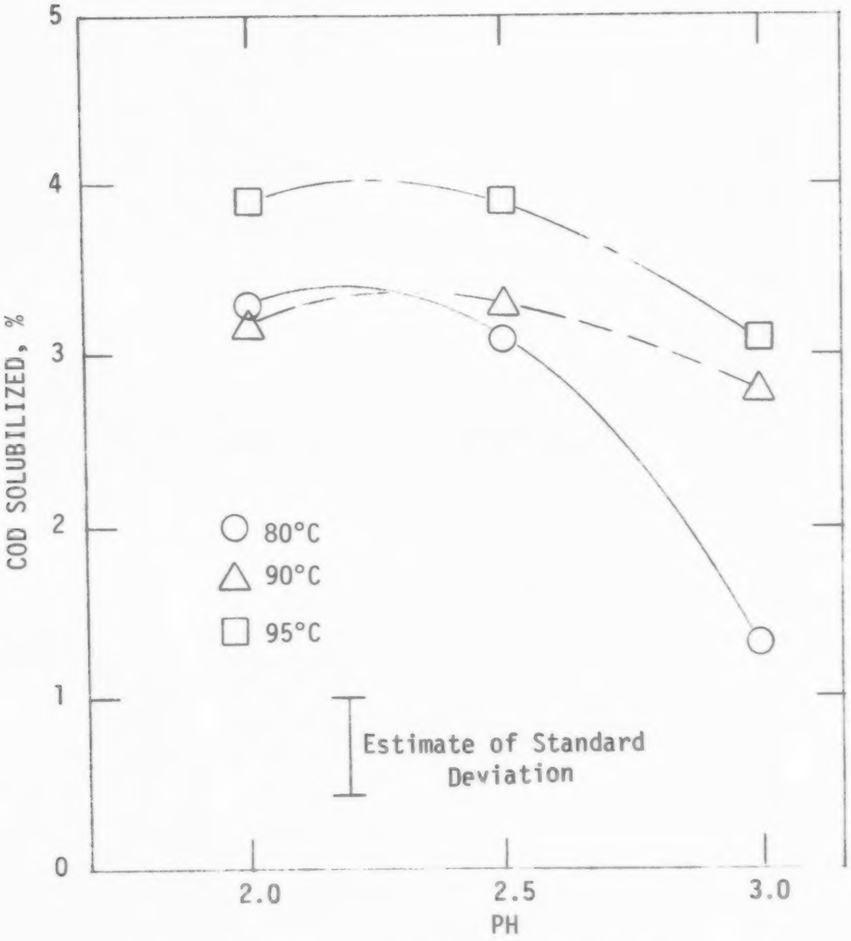

Figure 28. Effect of treatment conditions on the degree of COD solubilization for Fitchburg primary plus WAS.

TABLE 21. SUMMARY OF METALS SOLUBILIZATION FOR BROCKTON WAS

Metal	pH	No. of analyses	Average solubilization %	Standard deviation %	Range %
Zn	3.0	10	5	4	1-13
	2.5	15	28	21	4-81
	2.0	12	54	21	20-88
	1.5	8	78	18	62-100
	1.2	1	81	--	--
	1.0	1	78	--	--
Cr	2.5	3	3	4	1-7
	2.0	1	4	--	--
	1.5	7	33	5	29-44
Pb	2.5	3	4	6	0-11
	1.5	7	27	11	20-45
Cd	2.5	3	30	52	0-90
	2.0	2	0	--	--
	1.5	8	11	19	0-46
	1.2	1	49	--	--
	1.0	1	62	--	--

to questions on analytical accuracy. A number of samples were therefore submitted to the Municipal Environmental Research Laboratory of EPA for an independent check on the accuracy of Walden analyses. The results from the two analytical laboratories are compared in Appendix A. It is concluded that there is, in general, good agreement between the two laboratories and that the Walden results are at least as consistent as those obtained by EPA. The broad range in the degree of solubility at a given pH is probably attributabl to a difference between the bulk pH and the acidity at specific reaction sites (see Section 6.)

Destruction of Pathogens

Several analyses were conducted to assess the extent of pathogen destruction during hot acid treatment. Following treatment at pH 2.5, 95°C, and 10 minutes digestion time, samples of the treated sludge cake for each of the four sludges tested were submitted for bacteria analyses. Samples of each of the raw sludges were also submitted. Fecal coliform and fecal streptococcus were selected as indicators of pathogenic activity. The analytical results, shown in Table 22, indicate essentially complete destruction of both fecal coliform and fecal streptococcus

ASSESSMENT OF BENCH-SCALE OPTIMIZATION TESTS

The bench-scale process studies described above are useful for determining general process characteristics and estimating the technical and economic feasibility of the hot acid process. However, because of the biochemical changes that can occur in sludge, it is dangerous to draw unqualified conclusions on the basis of bench-scale tests. In addition, the process may behave differently under on-site, dynamic-flow conditions as opposed to the remote, static conditions investigated during this program. Thus the objective of bench-scale tests should be to indicate the potential of the process rather than to provide definitive process design data.

One of the major cost elements for the hot-acid process is the cost of acid required to reduce the pH of the sludge. Based on the results of Figure 12 and on a sulfuric acid cost of \$49.50/metric ton (\$45/short ton) for concentrated (98%) acid, the approximate acid cost as a function of pH would be:

pH	Acid Cost (\$/dmt solids)	Acid Cost (\$/dst solids)
3.0	2.40	2.20
2.5	4.35	3.95
2.0	5.80	5.30
1.5	10.10	9.20

TABLE 22. BACTERIAL ASSAYS FOR RAW AND HOT-ACID-TREATED SLUDGES

Sludge sample	Fecal Streptococcus, counts/100 ml	Fecal Coliform, counts/100 ml
Brockton WAS		
Raw	--	9.6×10^7
Hot acid treated	--	<100
Brockton primary plus WAS		
Raw	3.3×10^6	3.5×10^7
Hot acid treated	<100	<100
Fitchburg WAS		
Raw	--	4.2×10^8
Hot acid treated	--	<100
Fitchburg primary plus WAS		
Raw	--	2.8×10^8
Hot acid treated	--	<100

The acid cost for operating at pH 2.0 is quite reasonable and even at pH 1.5 the cost for acid is not highly excessive. The economics of the hot acid process will be considered in detail in Section 9, but based on the above costs, operation at pH's as low as 1.5 cannot be ruled out.

The question of relative acid demand of the liquid and solid fractions of the sludge was not directly addressed during the tests covered in this section. However, during the tests described in Section 6, a sample of Milwaukee WAS containing 1.7% solids was acidified to pH 1.9 and a sample of filtrate from the same sludge was acidified to the same pH. Based on the relative amounts of acid added, three-fourth of the acid demand was in the liquid fraction. For the raw sludge sample the acid demand calculated on a wet sludge basis (6.4 kg/wmt) is in good agreement with the data of Figure 13, but the acid demand calculated on a dry solids basis (375 kg/dmt) is nearly three times as great as the data of Figure 12 would indicate. These results indicate an appreciable acid demand for the liquid fraction and suggest that the acid requirement for the process can be significantly reduced by improved thickening of the sludge prior to hot acid treatment. During the tests described in this section, the solids concentration of the sludges generally ranged from 2.5 to 4.5%. Significantly higher solids concentrations have been reported (10) for both activated (6.5%) and mixtures of activated and primary (8.6%) sludges produced by flotation thickening without chemical additives.

A second technique that could be used to reduce acid costs is the use of waste acid rather than commercial sulfuric acid. Tests were conducted with a waste pickle liquor obtained from a local galvanizing shop. Two samples of Brockton waste activated sludge were adjusted to pH 2.5: one with concentrated sulfuric acid, the other with waste pickle liquor. The samples were digested at 95°C for 10 minutes prior to determining the settling, filtration, and centrifugation rates. Because of the very low solids concentration for the sludge sample tested (~1% solids) solid-liquid separation rates for the H_2SO_4-treated sample were quite rapid; however the waste pickle liquor appeared to significantly hinder the rate of solid-liquid separation. In addition the waste pickle liquor contained high concentrations of some heavy metals, e.g. 61,000 mg/l zinc. Considering the quantity of waste pickle liquor required for pH adjustment (23.5 ml/liter of sludge), it is possible to show by calculation that the amount of zinc remaining in the dewatered sludge (in the bound and interstitial water) is greater than the amount of zinc bound in the raw sludge even if the treated sludge is dewatered to impossibly high solids levels. Thus it would be necessary to either wash the cake solids or to select waste pickle liquors containing low concentrations of the more toxic heavy metals. Furthermore, heavy metals added with the waste pickle liquor would increase the cost for metals removal from the liquid stream prior to recycle to secondary treatment. Other sources of waste acid or low-cost acid were neither identified nor evaluated; however the results with waste pickle liquor suggest a cautious approach to the selection of substitute acids.

The solid-liquid separation tests provided preliminary information on the feasibility of three solids separation techniques (settling, filtration, and centrifugation) and on the effects of the primary process variables (pH, temperature, and time) on the rates of solid-liquid separation. Because of the difficulties inherent in using bench-scale tests to predict the performance of full-scale equipment, the bench-scale tests were used to select the perferred solid-liquid separation technique. Pilot scale tests were then conducted to develop quantitative design information for the selected technique. These results are presented and discussed in Section 7.

Table 23 summarizes the effects of the primary process variables on solid-liquid separation rates for the four sludges tested. For each sludge the variables having a significant effect, at the 95% confidence level, on solids separation rate are listed in order of decreasing significance. In general, pH is the variable with greatest influence on solid-liquid separation followed by temperature and then time. It is also of interest to note that the same variables are, in general, significant for both settling and centrifugation suggesting that the mechanism of solid-liquid separation is similar for these techniques and that their difference lies merely in the different gravitational accelerations used. The preferred levels of the operating variables for solids separation are also given in Table 23. For all sludges, the optimum pH is 2.5. The preferred temperature level is 90-95°C, with 95°C more generally appropriate, and the preferred time, which is not a critical variable, is 10-60 minutes, with 30 minutes representing a suitable compromise.

During the full-factorial optimization tests, the effect of the major process variables on solubilization of various sludge constituents was evaluated. Table 24 summarizes the variables found to be significant at the 95% confidence level. The variables are listed in order of decreasing significance for each sludge.

None of the variables investigated appeared to have a significant effect on the solubilization of suspended solids. This result is somewhat surprising since the suspended solids include both organics and metals, for which the variables investigated were determined to significantly affect solubilization. That is, as the pH is lowered, the solubilization of both organics and metals increase, and one would therefore expect an increase in suspended solids solubilization as the pH is lowered. Analyses conducted on the Fitchburg secondary sludge indicated that an average of 62.5% (range of 9 analyses: 60.1% - 64.6%) of the total solids in the raw sludge were volatile solids. Assuming the volatile solids consisted primarily of organics, the effect of pH on suspended organics and suspended solids should be similar. A possible explanation of this apparent anomalie lies in the assumption that the sulfate added as H_2SO_4 remains dissolved. If a portion of the sulfate becomes bound to the solids, then the percent solubilization as calculated by Equations (1), (3), and (4) would be too low, and the size of the error would increase with the amount of H_2SO_4 added. This would have the effect of canceling out the pH dependence for suspended solids solubilization. The lack of a pH dependence for suspended solids solubilization could also be explained by postulating that a decrease in pH increases either the volatilization or

TABLE 23. SUMMARY OF OPTIMIZATION TESTS FOR SOLID-LIQUID SEPARATION

	Significant variables			Preferred level of variable		
Sludge	Setting	Filtration	Centrifugation	pH	Temperature (C°)	Time (min)
Brockton 2°	pH temperature	pH temperature	pH temperature	2.5	95	--
Brockton 1°+2°	pH temperature (time)	pH	pH temperature	2.5	90	(10)
Fitchburg 2°	Temperature time pH	pH	Temperature time pH	2.5	95	60
Fitchburg 1° + 2°	pH (time)	none	--	2.5	--	(10)

Note: ( ) indicates marginally significant variable.

TABLE 24. SUMMARY OF SOLUBILIZATION RESULTS FOR OPTIMIZATION TESTS

Sludge	Significant variables SS solubilization	 COD solubilization	 Zn solubilization
Brockton 2°	None	pH	pH
Brockton 1°+2°	None	temperature pH (time)	pH
Fitchburg 2°	None	pH temperature time	pH time
Fitchburg 1°+2°	None	pH temperature	pH

Note: ( ) indicates marginally significant variable.

the fixation by solids of dissolved inorganics other than sulfate. However, from a practical point of view, it is really the solubilization of organic solids rather than total solids that is important in assessing the additional loading imposed on the treatment system by recycle. Thus the solubilization of inorganics could be viewed as being of little importance.

As shown in Table 24 the pH had a significant effect on the solubilization of COD and zinc for all sludges tested. The temperature was a significant variable for COD solubilization but not for zinc solubilization, and the time was not generally significant for either COD or zinc solubilization.

For optimum results it is desirable to minimize COD solubilization and maximize zinc solubilization. However, since the solubilization of both COD and zinc increases with decreasing pH, some compromise must be reached. Determination of the preferred pH level would require an economic optimization which would contain some very site-specific elements (such as the levels of metals in the sludge and the cost penalty for organics recycle).

From Table 24 it would appear that operation at low temperature could be used to minimize COD solubilization without affecting zinc solubilization. Although this approach may be of some use, the solid-liquid separation becomes more difficult as the temperature is decreased below 90°C. Again, an economic optimum would have to be defined to properly balance the opposing effects.

The bench-scale tests were useful in demonstrating that the hot acid process has the potential for solubilizing significant quantities of certain heavy metals. As shown in Table 21, solubilization ranged up to 100% for zinc, 90% for cadmium, 44% for chrome, and 45% for lead at pH's of 1.5 or above. In addition, results to be presented in Section 5 indicate good solubilization of nickel. While these results demonstrate the potential of the process for heavy metals removal, the degree of removal obtained in these tests was highly variable, e.g., cadmium solubilization at pH 2.5 varied from 0 to 90%. This suggests that either the characteristics of the particular sludge sample had a large influence on solubilization or there was some uncontrolled process variable (e.g. pH localization) responsible for the inconsistent results. Further tests were conducted to specifically evaluate heavy metals solubilization, and the results of these tests are presented and discussed in Section 6. In brief, high and consistent solubilization of heavy metals were obtained with various sludge samples during these latter tests. These results confirm the conclusion that the hot acid process has the potential for significant heavy metals removal from sludge.

Although the number of bacterial assays performed during the bench-scale tests were minimal, they confirmed the expectation that the hot acid process effectively destroys all pathogens. Pasteurization (exposure to high temperature for an adequate period of time) has long been recognized and used as an effective disinfection technique. The generally accepted conditions for sludge pasteurization (11)are a temperature of 70°C and holding times of 30 minutes to 1 hour. Table 25 (12)gives the holding times at temperatures of 70°C and below required to completely eliminate the various types of pathogens listed. It is evident from these data that the temperatures and times employed in the hot acid process would be more than sufficient to completely destroy all pathogens. In addition, the use of low pH should increase the rate of pathogen destruction.

Based on the bench-scale optimization tests and the above discussion of the state of advancement of the hot acid process, the potential advantages and disadvantages of the process are listed in Table 26. The unique potential advantage of the process is its ability to remove heavy metals from the sludge solids. The trade-off between advantages and disadvantages must eventually be reduced to an economic assessment of the hot acid process relative to other acceptable alternatives. A preliminary analysis of the process economics is given in Section 9.

The next step in the development of the process should be the design, installation, and operation of a transportable pilot system at various municipal wastewater treatment plants. Operation of a pilot system will provide data under dynamic flow conditions similar to a full-scale plant and will provide data unaffected by sludge age. The operation of a pilot system is considered essential to the further development, optimization, and verification of the hot acid process.

TABLE 25. EFFECT OF TIME AND TEMPERATURE ON THE SURVIVAL OF TYPICAL PATHOGENS FOUND IN SLUDGE* (12)

	Temperature °C				
Organism	50	55	60	65	70
	Minutes				
Cysts of *Entamoeba histolytica*	5				
Eggs of *Ascaris lumbricoides*	60	7			
Brucella abortus		60		3	
Corynebacterium diphtheria		45			4
Salmonella tyhposa			30		4
Escherichia coli			60		5
Micrococcus pyrogene var. aursus					20
Mycobacterium tuberculosis var. *promixis*					20
Viruses					25

*Pathogens completely eliminated at indicated time and temperature.

TABLE 26. POTENTIAL ADVANTAGES AND DISADVANTAGES OF HOT ACID TREATMENT

Potential advantages	Potential disadvantages
1. Improves solid-liquid separation rate and cake dryness	1. Solubilizes some organics
2. Removes toxic heavy metals from sludge solids	2. Requires heat and chemical addition
3. Destroys all pathogens	3. Requires corrosion-resistant materials of construction
4. Produces solids suitable for land application or animal-feed supplement	

SECTION 5

COMPARISON WITH ALTERNATIVE CONDITIONING PROCESSES

It is of interest to compare the performance of the hot acid process to the performance of alternative sludge conditioning processes. Bench-scale tests were conducted to compare the hot acid treatment with thermal treatment, ferric chloride treatment and polymer treatment. In addition, a literature review was performed to identify the characteristics of aerobic and anaerobic stabilization relative to the hot acid treatment process.

BENCH-SCALE COMPARISON OF CONDITIONING ALTERNATIVES

Bench-scale tests were conducted to directly compare various alternatives for conditioning the same sample of waste activated sludge. The various conditioning alternatives were compared both with respect to solid-liquid separation rates and to solubilization of sludge constituents.

Methods and Materials

The experimental apparatus and procedures for the hot acid treatment process were essentially identical to those described in Section 4. A one-liter sample of the sludge was treated at conditions of pH 2.5, 95°C, and 10 minutes digestion time.

For thermal conditioning, a 150-ml sample of sludge was placed in a high-pressure, stainless-steel, gas sampling cylinder fitted with a pressure gauge and thermocouple. The sealed cylinder was wrapped with heating tape and placed on a wrist-action shaker to provide mild agitation. The temperature during treatment was maintained within the range of 180-190°C and the time at temperature was 30 minutes. These conditions were selected on the basis of typical commercial practice (7) (30-40 minute detention time at temperatures of 170-205°C).

Ferric chloride was added as a 10% solution to a one-liter sample of raw sludge. In order to select the preferred dosage, preliminary tests were conducted with the same sludge to determine the effect of dosage on the solid-liquid separation rate.

A cationic polymer concentrate (Calgon Corp. WT-2860) was diluted to 10% of its initial concentration (concentrate = 15% solids) and added to a one-liter sample of sludge. As for ferric chloride, the polymer dosage was selected on the basis of preliminary tests at various dosages.

All tests were conducted on a single sample of Brockton waste activated sludge. The sample was obtained in the morning, and all tests were conducted during that same working day. The total solids concentration of the raw sludge was 2.5%.

The same apparatus and procedures as described in Section 4 were used to determine filtration and centrifugation characteristics. The sampling and analysis procedures were also similar to those described previously. Because of the small volume of sludge subjected to thermal treatment, the rates of settling after treatment were not compared.

Results and Discussion

Selection of Chemical Dosages--

Figures 29 and 30 show the rates of filtration and centrifugation, respectively for various dosages of ferric chloride. The dosages ranged from 0.016 to 0.80 g $FeCl_3$/g solids. Over this range, the rates of both filtration and centrifugation increased with dosage. However, the improvement in solid-liquid separation rate diminished beyond a dosage of 0.16 g/g solids, which was therefore selected as the preferred dosage for this sludge.

Similar tests were conducted with various polymer dosages ranging from 0.008 to 0.4 g of polymer concentrate per g solids. Filtration and centrifugation results for the various dosages are shown in Figures 31 and 32, respectively. The rate of solid-liquid separation for both filtration and centrifugation passed through a maximum at a dosage of 0.08 g/g solids. This dosage was therefore selected for subsequent tests.

It is of interest to note the chemical cost for the selected dosages of ferric chloride and polymer. Assuming a cost for ferric chloride (13) of \$110/metric ton (\$100/ton) the chemical cost corresponding to the selected dosage would be \$17.60/metric ton of solids (\$16/ton solids). Based on a book price for the polymer concentrate (personal communication with Calgon Corp., Pittsburgh, PA, June 1978) of \$1.06 kg (\$0.48 lb) in tank truck lots, the cost for polymer at the selected dosage would be \$85/dmt solids (\$77/dst solids). Because of the high cost, polymer treatment, at least with the selected polymer and dosage, would not be considered a viable alternative for the conditioning of this particular sludge.

Comparison of Solid-Liquid Separation Rates--

The rates of filtration following application of the various sludge conditioning treatments are shown in Figure 33. All of the conditioning processes gave a substantial increase in filtration rate relative to the untreated sludge. The thermal conditioning process produced very rapid filtration rates while the filtration rates for the hot acid, ferric chloride, and polymer treatments were roughly equal* but significantly less

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* It is noteworthy that the filtrate of the hot-acid-treated sample produced foam during this particular filtration test. This phenominon occurred sporadically from time to time and was accompanied by a significant retardation in filtration rate. It is postulated that, in the absence of foaming, the hot-acid sample would have filtered at least as rapidly as the polymer-treated sample.

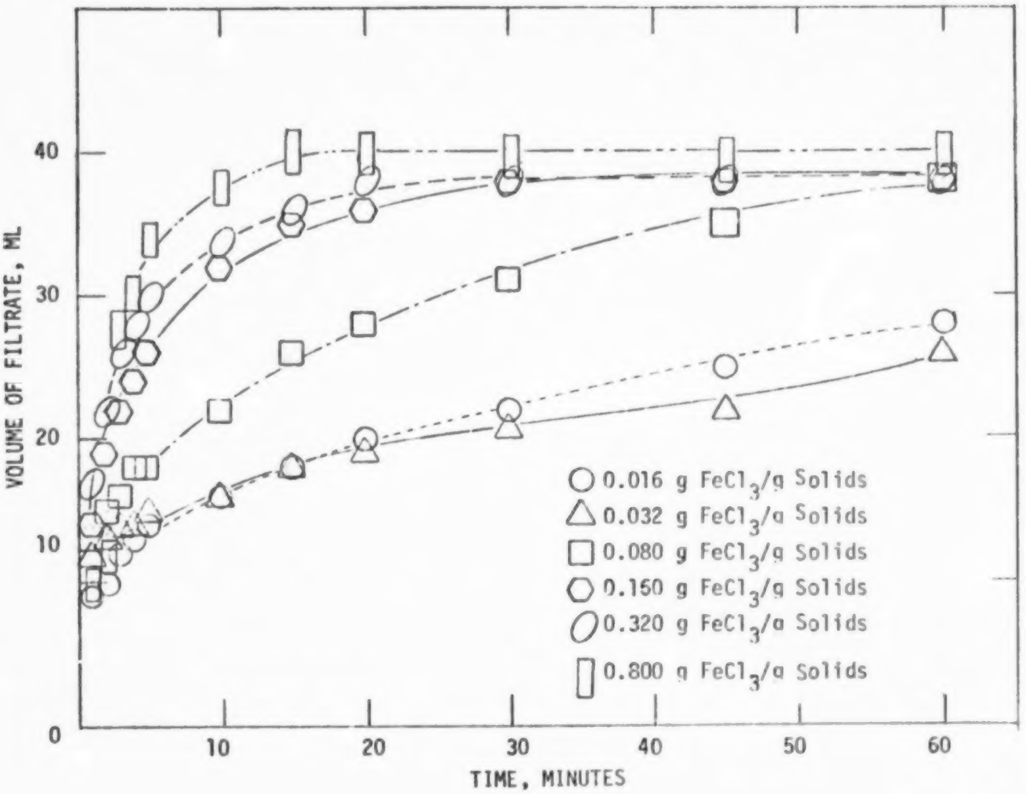


Figure 29. Effect of ferric chloride dosage on the filtration rate of hot-acid-treated WAS.

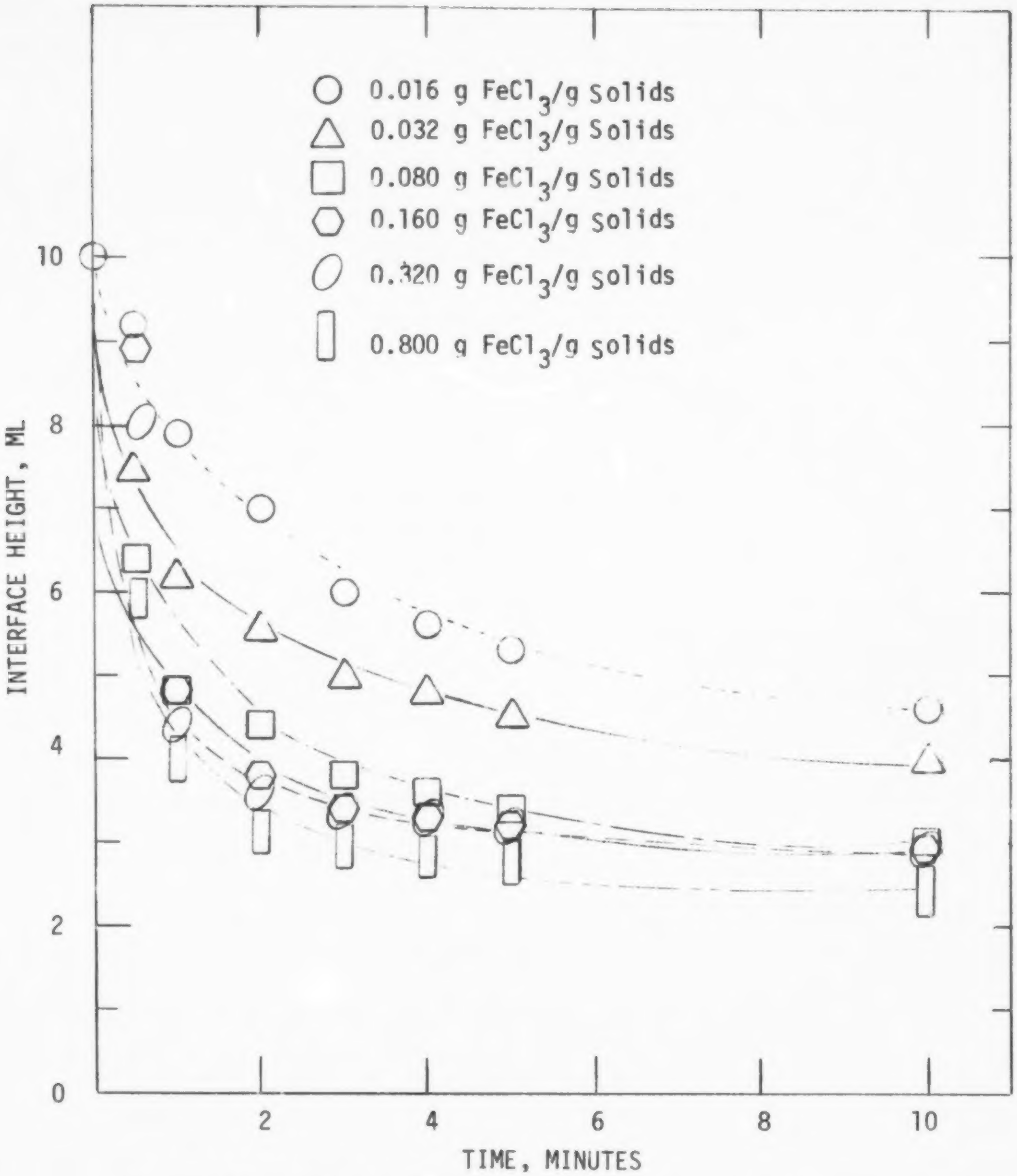


Figure 30. Effect of ferric chloride dosage on the centrifugation rate of hot-acid-treated WAS.

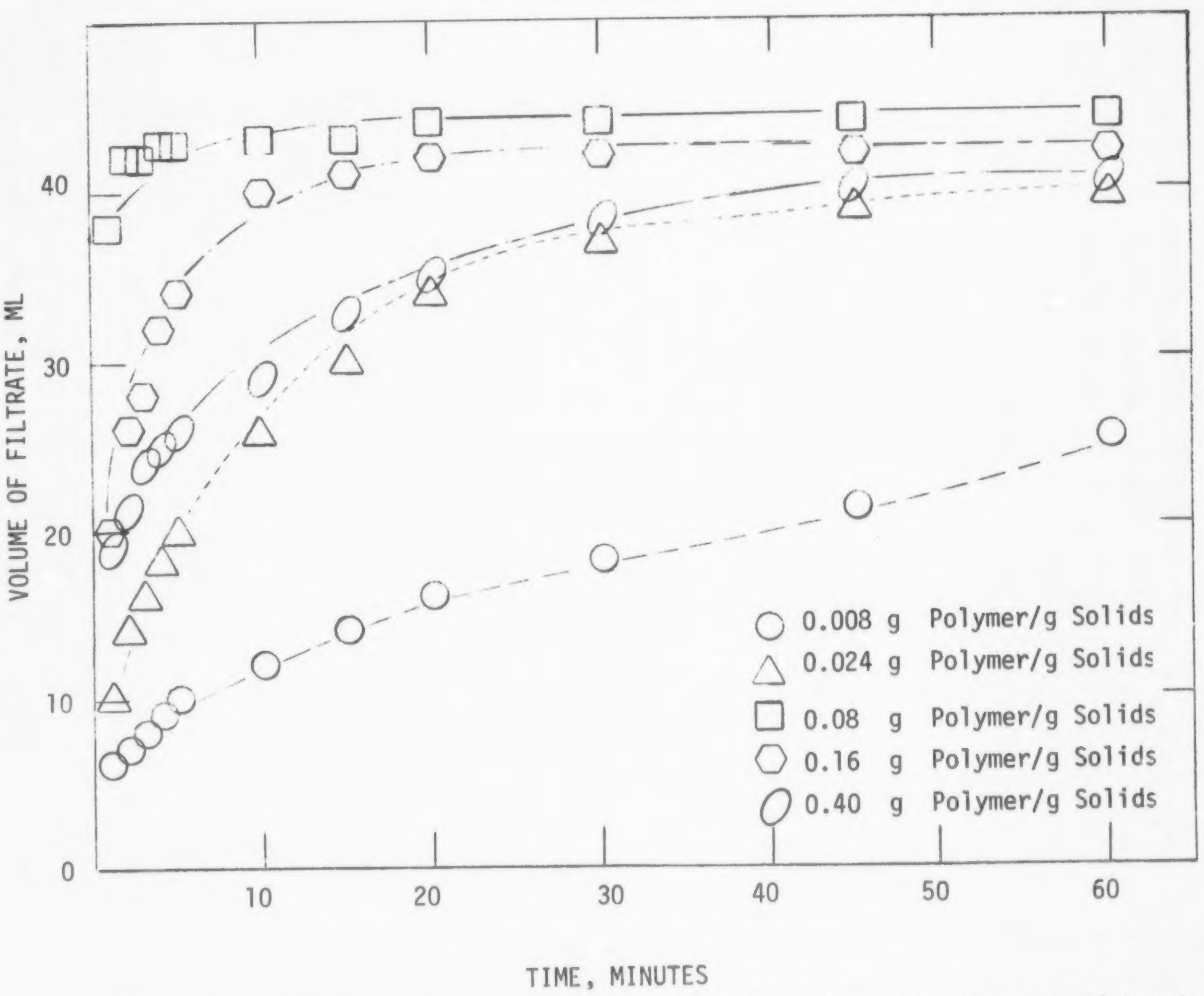


Figure 31. Effect of polymer dosage on the filtration rate of hot-acid-treated WAS.

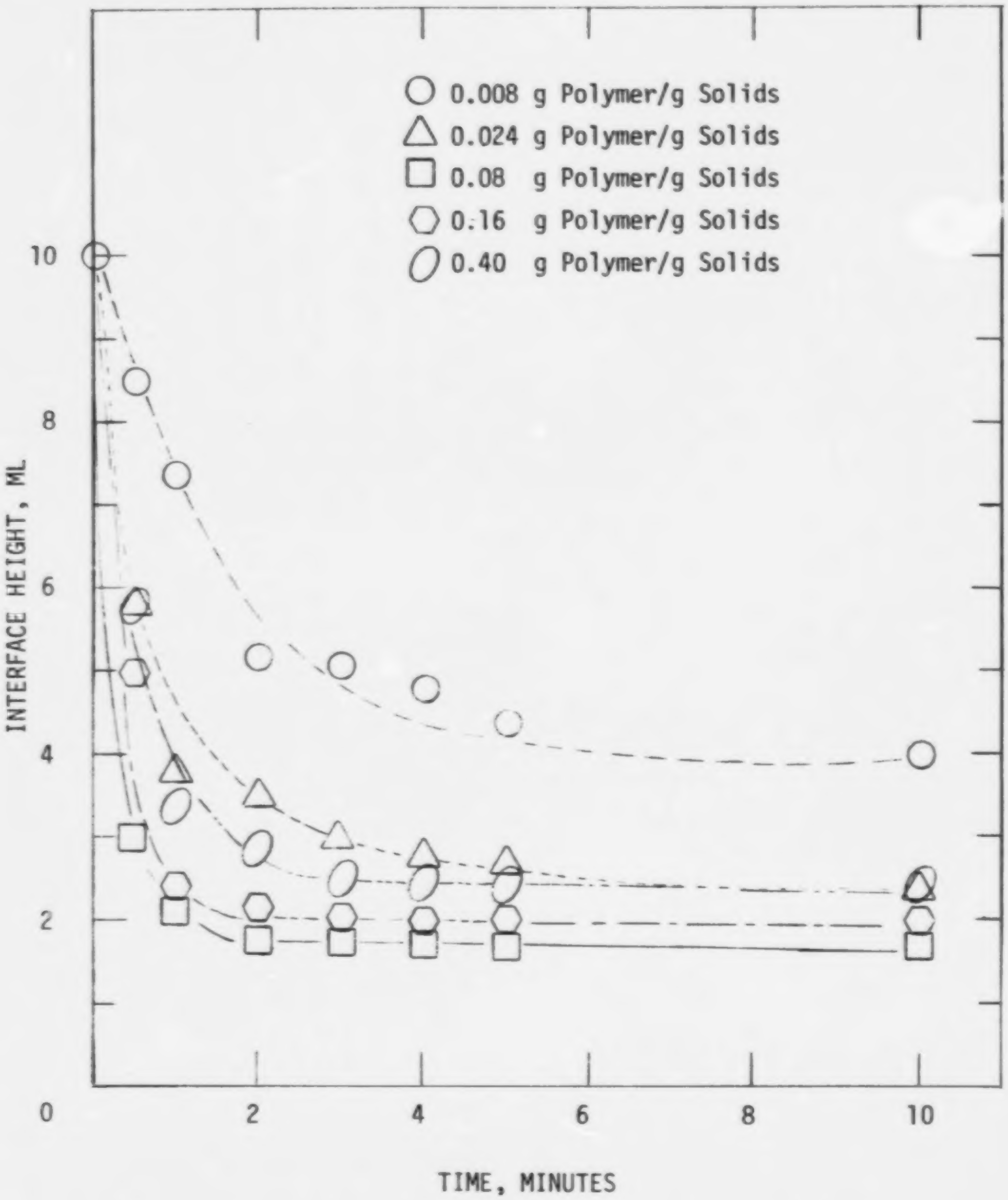


Figure 32. Effect of polymer dosage on the centrifugation rate of hot-acid-treated WAS.

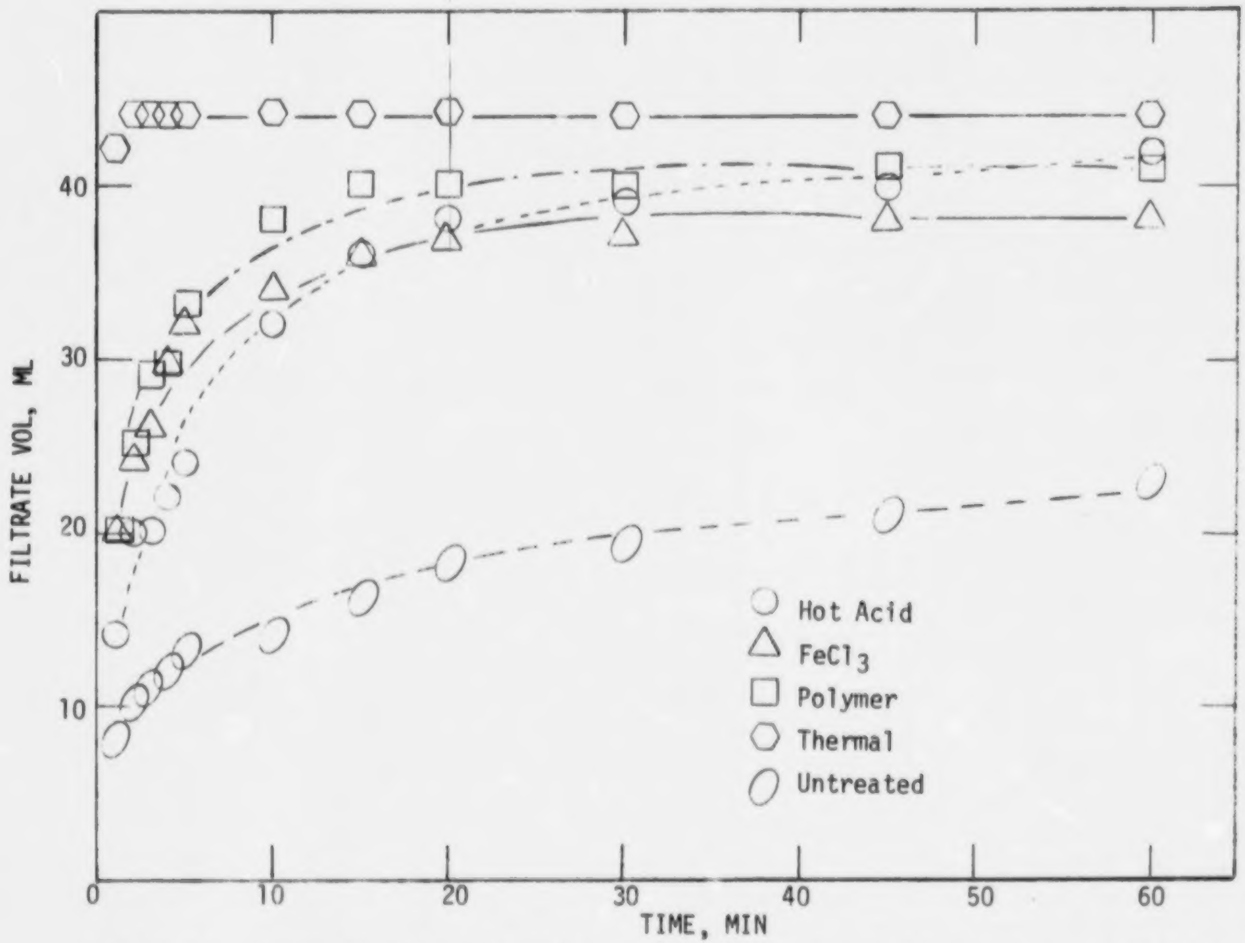


Figure 33. Comparison of filtration rates for WAS treated by various conditioning processes.

than for thermal treatment.

Rates of centrifugation following the various sludge treatments are shown in Figure 34. Again, all of the conditioning techniques produced a substantial improvement in centrifugation rate relative to the untreated sludge. Thermal treatment gave the best centrifugation rate followed by hot acid, polymer, and ferric chloride treatment in that order.

From these results, it can be concluded that the hot acid process produced solid-liquid separation rates which are at least as good as those produced by chemical conditioning. For centrifugation, the hot acid process can produce a sludge having dewatering characteristics superior to those of chemically conditioned sludge.

Solubilization of Sludge Constituents--

In addition to the rate of solid-liquid separation, the degree of solubilization of various sludge constituents is important in comparing alternative sludge conditioning processes. For sludge disposal by land application, the conditioning process should, ideally, solubilize the toxic heavy metals without significantly solubilizing organics, phosphorus, and nitrogen.

Table 27 gives the suspended solids and organics solubilizations obtained with the sample of Brockton waste activated sludge. The ferric chloride and polymer treatment produced no appreciable solubilization of suspended solids. The thermal treatment solubilized one-third of the solids while the hot acid process solubilized about one-tenth of the solids.

Since the supernatant from the sludge conditioning process must be treated, either directly or by recycle to the secondary treatment system, the organic loading of the filtrate is an important parameter in judging the merits of alternative conditioning processes. Both the BOD and COD of the various filtrates are shown in Table 27. Of the treated samples, the organic loading for ferric chloride treatment was the lowest. The higher BOD for the polymer-treated filtrate could have resulted from some residual polymer that was not removed with the solids. The BOD of the hot-acid-treated filtrate was only slightly higher than the BOD of the polymer-treated filtrate. Thermal treatment resulted in substantially greater organics solubilization than for the other processes. The high level of organics in the filtrate from the thermal process represents a significant additional load on the secondary treatment system. The recycle of thermal treatment liquors generally results in an increase in organic loading of approximately 20% on the secondary treatment system (7,14).

Table 28 further compares the solubilizations obtained with the hot acid and thermal processes. (The additional analyses of Table 28 were not performed for the ferric chloride and polymer treated samples since little, if any, solubilization was anticipated.) Comparing the results for heavy metals solubilization, the hot acid process solubilized significant quantities of zinc, cadmium and nickel but only small amounts of lead, chromium, and copper. The thermal process resulted in no significant solubilization of heavy metals except for nickel. The high nickel solubilization for the thermal process is questionable in the light of the low solubilization for other metals and in

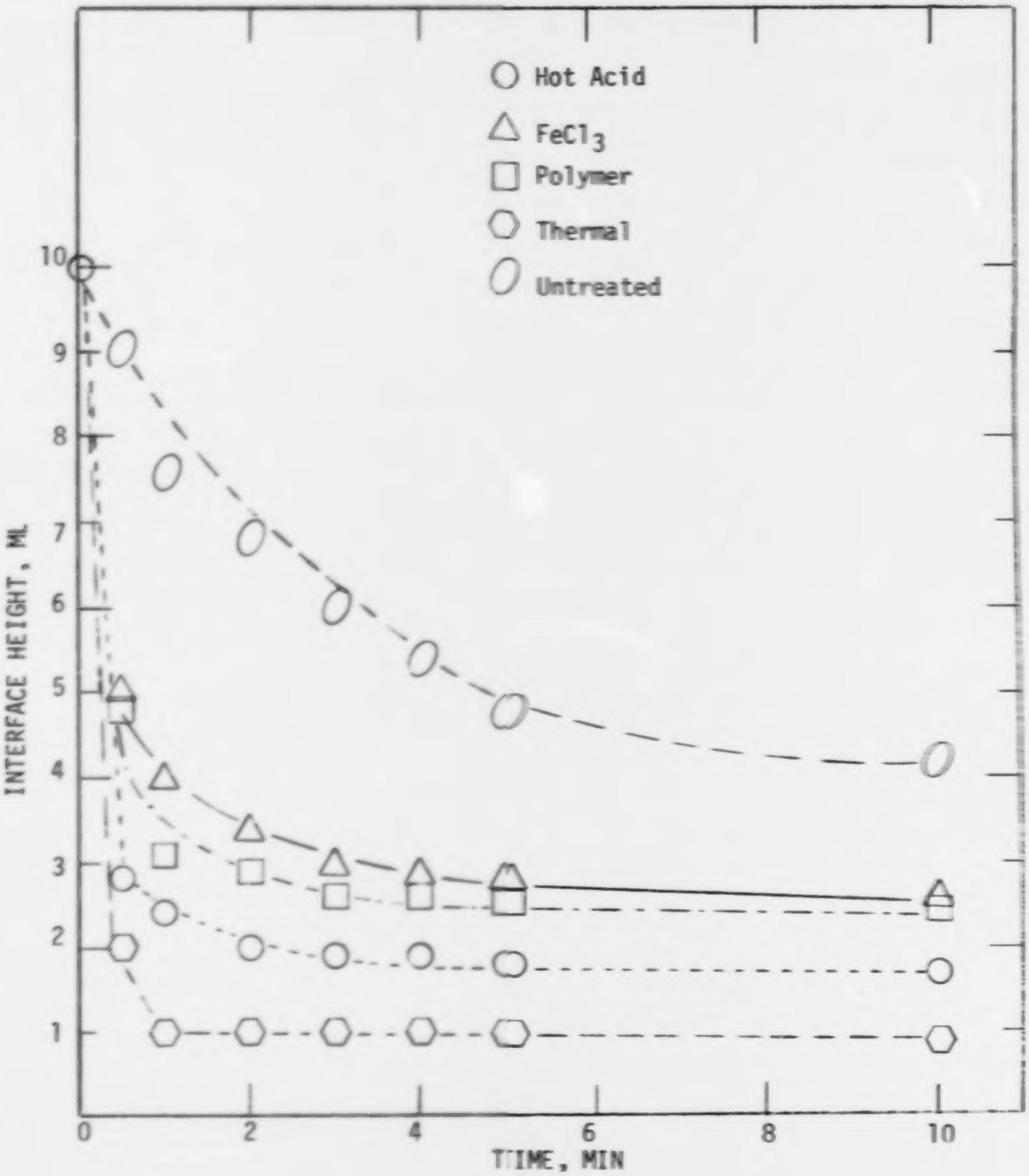


Figure 34. Comparison of centrifugation rates for WAS treated by various conditioning processes.

TABLE 27. SOLUBILIZATION OF SOLIDS AND ORGANICS FOR VARIOUS TREATMENT PROCESSES

Process	Suspended solids solubilization (%)	Filtrate BOD (mg/l)	Filtrate COD (mg/l)	COD solubilization (%)
No treatment	--	310	540	--
Hot acid	11	1,300	2,940	7.8
Thermal	34	5,600	11,300	27
Ferric chloride	1.5	610	830	0.9
Polymer	1.7	1,000	--	--

TABLE 28. COMPARISON OF SOLUBILIZATIONS FOR THE HOT-ACID AND THERMAL CONDITIONING PROCESSES

Sludge	Process	SS	COD	Zn	Cd	Ni	Cu	Cr	Pb	P	TKN
Brockton WAS	Hot acid	11	7.8	81	(90)	36	0	7	10	45	10
	Thermal	34	27	0.6	0	(69)	0	3	1	13	76
Milwaukee WAS	Hot acid	11	5	47	5	79	0	1.3	0	20	8.6

* Treatment conditions for hot acid process = pH 2.5, 95°C, and 10 min. digestion time. Treatment conditions for thermal process = 180-190°C for 30 min. digestion time.

( ) indicates questionable or uncertain results.

the light of previous research (5) which showed no significant metals solubilization (including nickel) for the thermal process. The high cadmium solubilization for the hot acid process is particularly noteworthy since cadmium is of considerable environmental concern. However, the 90% cadmium solubilization was not reproducible in these tests as noted in Section 4 (see Table 21).

The results for phosphorus and nitrogen (total Kjeldahl nitrogen) solubilizations are also shown in Table 28. For nitrogen, the hot acid process solubilized only 10% compared to 76% for the thermal process. The degree of phosphorus solubilization for the hot acid process (45%) was significantly greater for this sample than for other WAS samples tested and was considerably greater than the degree of phosphorus solubilization for the thermal process.

Table 28 also shows the solubilization results for hot acid treatment of Milwaukee WAS. The solubilizations of suspended solids and COD were essentially identical to those obtained for the Brockton sludge. Good solubilizations of zinc and nickel were obtained for the Milwaukee sludge, but the solubilization of cadmium was low. Copper, chromium, and lead were not solubilized. The 20% phosphorus solubilization was more typical than for the Brockton sludge, and the nitrogen solubilization was about the same as for the Brockton sludge.

These solubilization results indicate that the hot acid process exhibits a number of advantages over thermal treatment. Relative to thermal treatment, the hot acid process:

-- produces lower solubilization of solids,
-- produces lower solubilization of organics,
-- produces lower solubilization of nitrogen, and
-- has better potential for removal of toxic heavy metals.

As a result of these advantages, the sludge produced by the hot acid process should be much more desirable for land application than sludge from a thermal treatment process.

CHARACTERISTICS OF BIOLOGICAL STABILIZATION

Of the various stabilization processes, anaerobic and aerobic digestion are the most widely used. Although experiments were not conducted with these processes, it is possible to make some general comparisons between these processes and the hot acid and thermal treatment processes.

Solid-Liquid Separation

Both anaerobic and aerobic digestion improve the dewaterability of the treated sludge (generally a mixture of primary and waste activated sludge), but the degree of improvement is not sufficient to permit direct dewatering of the digested sludge. Chemical conditioning of digested sludge, with lime, ferric, and/or polymer is generally required prior to dewatering.

Estimates of chemical requirements (15) (based on experience at different treatment plants in the United States) are shown for raw and anaerobically digested sludge in Table 29. The chemical cost for conditioning anaerobically digested sludge can considerably exceed that for raw sludge because the high concentration of carbonates produced during anaerobic digestion inhibits coagulation of the solids with ferric chloride. Similarly, aerobically digested sludges generally have been found to have poor dewatering characteristics (16).

Reduction of Solids

Both anaerobic and aerobic digestion reduce the volume of solids requiring disposal. In anaerobic digestion organic solids are converted to volatile organic acids which are, in turn, converted primarily to methane and carbon dioxide. Thus a portion of the raw sludge solids is converted to a gas mixture which can be recovered and used for fuel (heating value (15) 5,300-7,100 kcal/m^3 [600-800 Btu/ft^3]). Anaerobic digestion can typically achieve (on a dry basis) a 25% reduction in sludge total solids and 35% reduction in sludge volatile solids (15).

Aerobic digestion also reduces the volume of solids requiring disposal. The primary mechanism for solids reduction is endogenous respiration in which cellular matter is biologically oxidized. Aerobic digestion can achieve (on a dry basis) total solids reductions of 25%-35% with corresponding volatile solids reductions of 40%-50% (15).

Pathogen Destruction

Both aerobic and anaerobic digestion reduce the concentration of pathogenic organisms. For anaerobic digestion, digestion conditions are not lethal to most pathogens, but are not conductive to multiplication. Thus pathogen destruction appears related to a natural die-off with time (15). Anaerobic digestion has been rated (11) as "fair" (1 to 3 logs reduction) for destruction of pathogenic bacteria (Salmonella) and "poor" (less than 1 log reduction) for viruses. Aerobic digestion has been rated as "poor" for pathogen removal; however the potential for virus removal was unknown.

Supernatant Quality

The quality of the supernatants from anaerobic and aerobic treatment (15) are compared in Table 30. The variability in the parameters listed results primarily from differences in the digester designs and the efficiency of solids separation. For comparison purposes, the supernatant quality from thermal treatment is also shown in Table 30. In general, aerobic digestion produces the highest quality supernatant followed in order by anaerobic digestion and thermal treatment. Undoubetedly, much of the organic loading of the supernatants from biological digestion arises from the presence of biological solids. On the other hand, the organics loading of the thermal treatment liquor is largely dissolved (compare results of Table 27) and represents a much more difficult treatment problem than the biological supernatants.

TABLE 29. ESTIMATED CHEMICAL CONDITIONING DOSAGES FOR VACUUM FILTRATION (16)

Type of sludge	CaO dose (kg/dmt)	$FeCl_3$ dose (kg/dmt)	Polymer dose (kg/dmt)	CaO + $FeCl_3$ cost		Polymer cost	
				($/dmt)	($/dst)	($/dmt)	($/dst)
Raw (primary + WAS)	100	26	9	6.58	5.98	6.54	5.94
Anaerobically digested (primary + WAS)	186	55	18	13.24	12.02	13.08	11.55

Note: CaO cost = $0.0275/kg ($0.0125/lb)
$FeCl_3$ cost = $0.147/kg ($0.067/lb)
Polymer cost = $0.727/kg ($0.33/lb)

TABLE 30. COMPARISON OF SUPERNATANT QUALITY FOR VARIOUS SLUDGE TREATMENT TECHNIQUES

	Anaerobically digested	Aerobically digested		Thermally treated
		Average	Range	
Suspended solids	5,000-15,000	3,400	46-11,500	--
BOD_5, mg/l	1,000-10,000	500	9- 1,700	5,000-15,000
COD, mg/l	3,000-30,000	2,600	288- 8,140	10,000-30,000
Ammonia as NH_3, mg/l	500- 1,000			500-700
Total phosphorous P, mg/l	300- 1,000	98	19- 241	150-200

Heavy Metals Removal

Anaerobic and aerobic digestion do not release any significant quantity of heavy metals from the sludge solids. In fact, it has been found(17) that soluble metals are incorporated into the biomass during anaerobic digestion. Measurements have been made(18) on the extractability of heavy metals from anaerobically and aerobically digested sludges using water and EDTA. The water extractability of cadmium, lead, and zinc remained uneffected by anaerobic digestion, while nickel and copper became less extractable. The water extractability of chromium, copper, and zinc increased following aerobic digestion, but that of cadmium, nickel, and lead remained unchanged. However, in all cases the water extractability of metals remained low, i.e., at a level of less than 10 percent of the EDTA extractability of the metals. Therefore it is concluded that neither anaerobic nor aerobic digestion result in any significant removal of heavy metals from sludge.

DISCUSSION AND CONCLUSIONS

The sludge treatment processes considered above fall into four main categories:

- -- chemical treatment (polymer or inorganic chemicals),
- -- biological digestion (anaerobic or aerobic),
- -- thermal treatment, and
- -- hot acid treatment.

These four categories are discussed below with respect to process performance characteristics. The economics of the various treatment alternatives are considered in Section 9.

Considering current recommendations for the disposal of wastewater sludges(1), it appears to be necessary to stabilize the sludge (with treatment equivalent to anaerobic digestion) prior to disposal by land application or sanitary landfill. Since ocean dumping is being phased out, incineration is the only major disposal technique which does not require prior sludge stabilization. However, incineration is a volume reduction technique rather than an ultimate disposal technique and, as such, should be considered as a stabilization rather than a disposal process. Thus the need for stabilization prior to ultimate disposal appears to be quite general. Chemical treatment, as generally practiced for dewatering, will not produce a disposable sludge since the process does not stabilize the sludge solids.

As noted above, biological digestion produces a stabilized sludge, but the sludge cannot generally be dewatered without chemical conditioning. Thus biological stabilization requires chemical conditioning, and chemical conditioning requires biological (or other) stabilization. On the other hand, both thermal treatment and, ideally, hot acid treatment produce a stabilized, dewaterable sludge in a single processing step. Therefore, in comparing various sludge conditioning alternatives, three categories may be considered:

- -- biological stabilization with chemical conditioning,
- -- thermal treatment, and
- -- hot acid treatment.

The performance characteristics of the above alternatives are compared in Table 31. While this type of comparison can highlight general characteristics of the alternative processes, the final selection must be based on an economic assessment which includes consideration of ultimate disposal. Nevertheless it can be concluded from Table 31 that the hot acid process compares quite favorably to the other two alternatives.

TABLE 31. COMPARISON OF SLUDGE CONDITIONING ALTERNATIVES

Performance characteristic	Biological/ chemical treatment	Thermal treatment	Hot acid treatment
Solids separation	Good	Excellent	Good (?)
Pathogen destruction	Fair	Excellent	Excellent
Putrefaction potential	Good	Fair	Fair (?)
Supernatant organics (dissolved)	Good	Poor	Fair
Heavy metals removal	Poor	Poor	Good
Solids nitrogen	Good	Poor	Good

SECTION 6

RE-EVALUATION OF HEAVY METALS SOLUBILIZATION

As discussed in Section 4 and 5 the hot acid process has several potential advantages over alternative conditioning techniques. The most unique advantage is its potential for solubilization and removal of toxic heavy metals. Of particular importance is the removal of cadmium because of its tendency to accumulate in certain agricultural crops. The degree of cadmium solubilization obtained in previous tests (see Table 21) was quite erratic, ranging from 90% in one test at pH 2.5 to essentially zero in other tests conducted at the same pH.

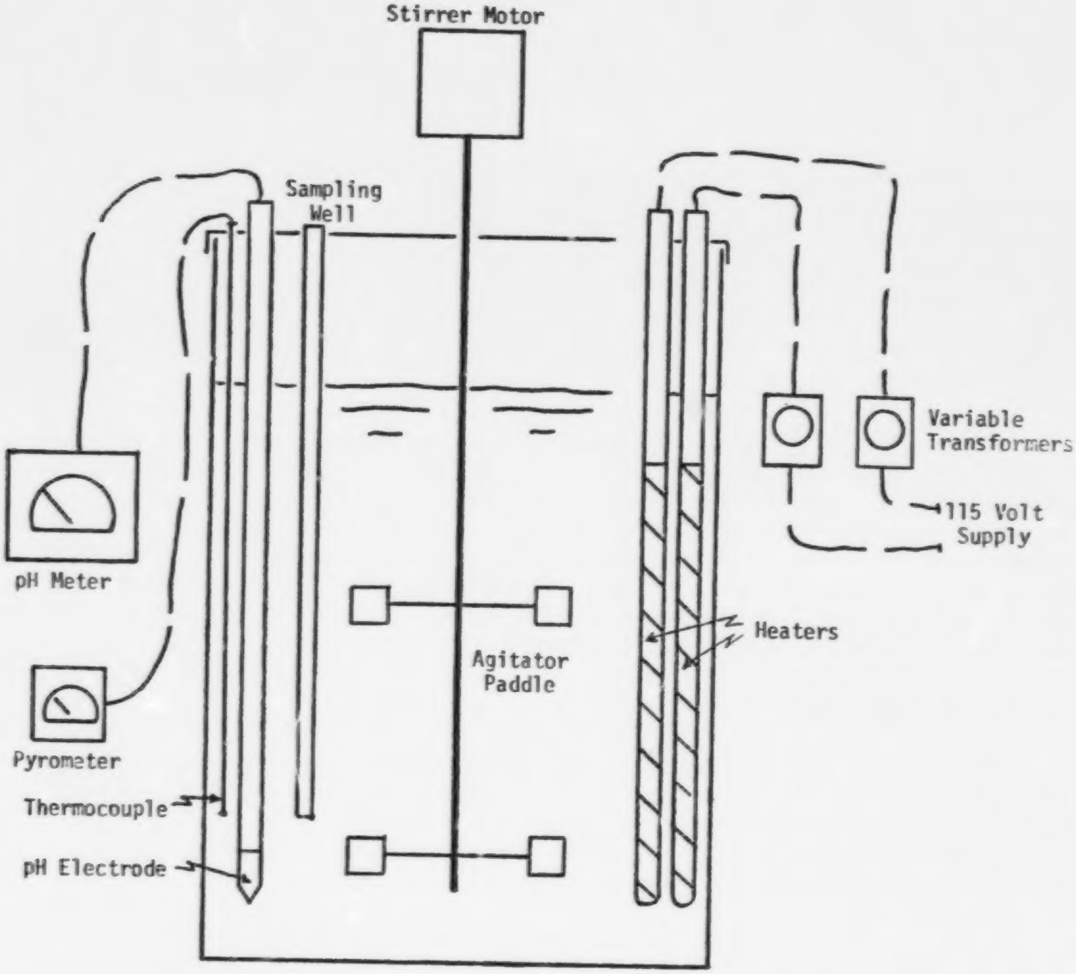
Additional tests were undertaken to focus primarily on heavy metals solubilization and to attempt to resolve the erratic results observed in previous tests. Several variables were investigated for their effect on the degree of solubilization. These included: amount of acid added, stirring speed, heating before acidification vs. acidification before heating, digestion time, and source of sludge. A different digestion apparatus was used for these tests which permitted the use of larger sludge samples, better control of operating conditions, and wider variability of stirring speed.

METHODS AND MATERIALS

A schematic diagram of the digestion apparatus is shown in Figure 35. The digestion was conducted in a 14-liter fermenter constructed of pyrex glass with a stainless-steel top plate and internals. The reactor contained four vertical baffles, a turbine mixer, a single orifice sparger, pH/reference electrodes, a thermocouple well, a sample withdrawal tube, and two 1000-watt Vycor immersion heaters. With two heaters each operated at 110 volts, the time required to heat 8 liters of sludge to 95°C was about 35 minutes, and rapid stirring (600 rpm) was used to prevent local overheating of the sludge. All tests were conducted at 95°C.

In previous tests the pH of the sludge was always adjusted to the desired level prior to heating; however in some of the tests reported in this section, acid was added after heating to the digestion temperature. This necessitated the measurement of pH at elevated temperatures, which proved to be somewhat inaccurate. For these samples the pH values reported in this section were measured after the digested sample had cooled to room temperature.

Following digestion a sample of the treated sludge was obtained for


Stirrer Motor
Sampling Well
Variable Transformers
115 Volt Supply
pH Meter
Heaters
Agitator Paddle
Pyrometer
Thermocouple
pH Electrode

NOTE: 4 VERTICAL BAFFLES NOT SHOWN

Figure 35. Schematic diagram of digestion apparatus used to evaluate heavy metals solubilization.

analysis. The sample was allowed to cool and was divided into two portions. One portion was submitted for analysis without further treatment (treated sludge sample). The other sample was centrifuged and the centrate passed through a 0.45μ Millipore filter before submission for analysis (treated sludge filtrate sample). A similar treatment was applied to a sample of the raw sludge to give a raw sludge sample and a raw sludge filtrate sample. All samples were preserved by refrigeration until analysis, and analytical work on the samples was initiated within 24 hours. The same analytical techniques and calculational procedures as described in Section 4 were used for these tests.

Fresh samples of WAS were obtained for all tests (with the exception of a few tests conducted on Milwaukee WAS). The samples were obtained in the morning and the tests were conducted on the afternoon of the same day.

RESULTS AND DISCUSSION

The experiments conducted to characterize heavy metals solubilization were divided into two groups. For the first group, all tests were conducted with fresh Brockton WAS to evaluate the effects of various operating conditions. For the second group of tests, the preferred operating conditions were fixed and sludges from different cities were evaluated. The detailed test data, including test conditons, analytical results, and calculated solubilizations, are given in Table 32.

A number of operating variables were investigated in an attempt to define the factors controlling cadmium (and other constituent) solubilizations, these included:

--apparatus (14-liter fermenter, designated 14-LF vs. one-liter graduated cylinders, designated 1-LGC and described in Section 4);
--stirring speed (600 rpm vs. 60 rpm using 14-LF; stirring speed for 1-LGC was 60 rpm);
--order of acid heat addition (acid added before heating vs. heating before acid addition);
--digestion time (30 min.vs. 60 min. not including heat-up time); and
--amount of acid added.

Tests were first conducted to compare the 14-liter fermenter (operated at 600 rpm with acid addition after heating and a digestion time of 30 minutes) to the one-liter graduated cylinders (operated at 60 rpm with acid addition before heating and a digestion time of 30 minutes). These tests were somewhat inconclusive because of the difficulty in properly adjusting the pH of hot sludge. Therefore, in the first two tests the amount of acid added per unit weight of sludge was different for the two digesters. This variable was determined to strongly influence the degree of solubilization and could have hidden the effects of the other variables such as digester configuration, degree of mixing, order of acid-heat addition, etc. In the third test the amount of acid added to the two samples was the same but was insufficient to produce any significant solubilization of cadmium. The solubilization of zinc was greater for the 14-liter fer-

TABLE 32. EFFECT OF TREATMENT CONDITIONS ON THE DEGREE OF SOLUBILIZATION OF HEAVY METALS AND OTHER SLUDGE CONSTITUENTS.

Line	Date	Conditions[*]	Raw solids (wt %)	H_2SO_4 added (ml/l)	Acid usage kg/dmt	pH @ 25°C	Digestion time (min)
1	2/28/78	Raw sludge	3.42	-	-	6.01	-
2	2/28/78	14-LF, 600, HBA	3.42	4.88	261	1.90	30
3	9/5/78	Raw sludge	2.50	-	-	6.51	-
4		1-LGC, 50, ABH	2.50	3.00	220	2.20	30
5		14-LF, 600, HBA	2.50	5.63	412	1.65	30
6	9/11/78	Raw sludge	4.03	-	-	6.08	-
7		1-LGC, 60, ABH	4.03	2.50	112	2.14	30
8		14-LF, 600, HBA	4.03	2.94	132	2.04	30
9	9/19/78	Raw sludge	3.75	-	-	6.39	-
10		1-LGC, 60, ABH	3.75	2.20	107	2.15	30
11		14-LF, 600, HBA	3.75	2.20	107	2.44	30
12	9/25/78	Raw sludge	3.28	-	-	6.37	-
13		14-LF, 60 HBA	3.28	2.50	140	2.07	30
14		14-LF, 600, HBA	3.28	2.50	139	2.05	30
15	10/2/78	Raw sludge	3.40	-	-	6.58	-
16		14-LF, 600, ABH	3.40	2.28	122	2.10	30
17		14-LF, 600, HBA	3.40	2.28	122	2.10	30
18	10/10/78	Raw sludge	3.27	-	-	6.00	-
19		14-LF, 600, HBA	3.27	1.1	62	3.50	30
20		14-LF, 600, HBA	3.27	2.30	129	2.00	30
21		14-LF, 600, HBA	3.27	2.30	129	2.00	60
22	10/16/78	Raw sludge	3.57	-	-	6.70	-
23		14-LF, 600, HBA	3.57	3.28	168	1.75	30
24		14-LF, 600, HBA	3.57	3.74	192	1.55	30
25		14-LF, 600, HBA	3.57	4.29	220	1.57	30
26		14-LF, 600, HBA	3.57	4.88	250	1.33	30
27	10/23/78	Raw Sludge	3.62	-	-	6.36	-
28		Opt[†](Brockton WAS)	3.62	4.67	236	1.47	60
29	10/30/79	Raw Sludge	1.59	-	-	6.25	-
30		Opt[†](Fitchburg WAS)	1.59	2.74	315	1.80	60
31	11/6/78	Raw Sludge	4.87	-	-	6.10	-
32		Opt[†] (Lawrence WAS)	4.87	7.65	288	1.78	60
33	11/14/78	Raw sludge	1.70	-	-	6.85	-
34		Opt[†] (Milwaukee WAS)	1.70	2.94	317	1.96	60
35		Opt[†] (Milwaukee WAS)	1.70	2.50	269	2.40	60

[*] Condition Code: 14-LF = 14-liter fermenter; 1-LGC = one-liter graduated cylinder;600 or 60 = stirring speed in rpm; HBA = heat before acid; ABH = acid before heat.

[†] Optimum conditions for sludges from various cities were: use of 14-liter fermenter, 600 rpm agitation, acid addition before heating, and 60 minute digestion time.

TABLE 32. EFFECT OF TREATMENT CONDITIONS ON THE DEGREE OF SOLUBILIZATION OF HEAVY METALS AND OTHER SLUDGE CONSTITUENTS (continued)

	Concentrations in wet sludge (mg/l)															
	Solids**		COD		Cadmium		Zinc		Nickel		Copper		Chromium		TKN	
Line	Total	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis	Tot	Dis
1	34,200	1,000	-	-	0.88	<0.2	33	<0.5	1.0	<1.0	-	-	131	<1	-	-
2	34,400	8,840	-	-	0.92	0.90	33	32	1.1	1.1	-	-	143	48	-	-
3	25,000	510	45,100	640	0.6	<0.2	53	<0.5	<1	<1	28	<1	231	<1	-	-
4	39,183	5,183	59,700	6,750	0.8	0.3	72	56	2.3	1.7	36	<1	280	33	-	-
5	30,117	2,717	54,100	10,900	0.6	0.7	61	48	<1	<1	34	3.1	264	91	-	-
6	40,300	790	46,700	500	1.0	<0.1	54	0.5	1.0	<1	28	<1	200	<1	-	-
7	41,053	6,353	5,200	5,050	1.2	0.2	61	31	1.6	<1	32	<1	212	11	-	-
8	39,786	7,786	54,100	7,350	1.1	0.5	60	36	1.6	<1	33	<1	212	24	-	-
9	37,500	700	47,700	415	1.2	<0.2	69	<0.5	1.4	<1	38	<1	300	<1	-	-
10	39,953	5,953	51,400	5,090	1.1	<0.2	63	16	1.6	1.1	39	<1	290	17	-	-
11	41,574	8,474	56,800	8,050	0.9	<0.2	52	34	1.0	<1	35	<1	290	9.1	-	-
12	32,800	550	55,200	460	0.9	<0.2	56	<0.5	<1	<1	30	<1	280	<1	-	-
13	49,453	11,653	57,000	8,430	1.2	0.5	68	50	1.6	1.3	38	<1	350	23	-	-
14	37,053	7,853	53,600	6,950	1.0	0.4	52	35	1.5	1.2	30	<1	260	15	-	-
15	34,000	640	40,000	140	0.89	<0.2	56	<0.5	1.1	<1	29	<1	320	<1	-	-
16	39,043	5,143	45,000	3,500	0.86	0.7	55	64	1.1	<1	28	<1	320	14	-	-
17	37,043	8,043	46,000	6,000	0.74	<0.2	49	25	1.6	1.0	25	<1	290	18	-	-
18	32,700	760	38,000	450	0.76	<0.2	37	<0.5	<1	<1	21	<1	200	<1	-	-
19	36,267	4,617	42,000	4,300	0.76	<0.2	36	0.6	<1	<1	21	<1	200	1.9	-	-
20	35,600	6,900	43,000	6,400	0.79	<0.2	63	20	<1	<1	19	<1	200	22	-	-
21	-	-	-	-	0.81	0.49	-	-	-	-	-	-	-	-	-	-
22	35,700	628	43,000	660	0.85	<0.2	50	<0.5	<1	<1	27	<1	330	<1	-	-
23	33,405	7,605	41,000	72,000	0.74	0.6	42	32	<1	<1	25	<1	300	58	-	-
24	-	-	-	-	0.57	0.37	37	24	-	-	-	-	-	-	-	-
25	-	-	-	-	0.66	0.68	47	33	-	-	-	-	-	-	-	-
26	-	-	-	-	0.77	0.70	46	34	-	-	-	-	-	-	-	-
27	36,200	624	34,000	420	0.87	<0.1	44	<0.5	0.9	<1	24	<1	232	<1	6,000	100
28	42,576	6,776	51,000	7,900	0.97	0.85	52	44	1.1	0.8	29	0.9	271	120	7,600	2,100
29	15,900	268	14,000	79	<0.1	<0.1	8.7	0.5	8.3	<1	28	<1	49	<1	580	7.2
30	15,043	4,370	13,000	2,500	0.1	0.1	10	8.3	8.3	7.1	27	22	62	26	870	220
31	48,700	1,050	36,000	1,800	0.34	<0.2	33	<0.5	3.3	<0.5	194	<1	48	<1	2,300	160
32	49,098	14,098	65,000	10,000	0.38	0.40	34	36	3.1	3.2	174	84	46	37	2,400	1,100
33	17,000	1,340	18,000	900	2.3	<0.1	32	<0.5	4.6	<0.5	8.2	<1	120	<1	714	82
34	17,888	4,088	17,000	3,800	2.3	2.1	33	33	4.3	3.9	8.2	6.4	100	44	990	240
35	-	-	-	-	3.2	2.8	44	41	41	6.6	4.9	11	1	-	-	-

** Values corrected for sulfate added as H_2SO_4 using procedures of Section 4.

TABLE 32. EFFECT OF TREATMENT CONDITIONS ON THE DEGREE OF SOLUBILIZATION OF HEAVY METALS AND OTHER SLUDGE CONSTITUENTS. (concluded)

	% Solubilization							
Line	Solids	COD	Cadmium	Zinc	Nickel	Copper	Chromium	TKN
1	-	-	-	-	-	-	-	-
2	23.5	-	97.8	97.0	100.0	-	33.6	-
3	-	-	-	-	-	-	-	-
4	12.1	10.3	37.5	77.8	73.9	0	11.8	-
5	7.5	19.2	100.0	78.7	-	9.1	34.5	-
6	-	-	-	-	-	-	-	-
7	13.8	8.8	12.5	50.4	0	0	5.2	-
8	17.9	12.8	41.8	59.7	0	0	11.3	-
9	-	-	-	-	-	-	-	-
10	13.4	9.2	0	25.4	68.8	0	5.9	-
11	19.0	13.5	0	65.4	0	0	3.1	-
12	-	-	-	-	-	-	-	-
13	22.7	14.1	41.7	73.5	81.3	0	6.6	-
14	20.0	12.2	40.0	67.3	80.0	0	5.8	-
15	-	-	-	-	-	-	-	-
16	11.7	7.5	81.4	100	0	0	4.4	-
17	20.3	12.8	0	560	62.5	0	6.2	-
18	-	-	-	-	-	-	-	-
19	10.9	9.3	0	1.6	0	0	1.0	-
20	17.6	14.0	0	31.7	0	0	11.0	-
21	-	-	60.5	-	-	-	-	-
22	-	-	-	-	-	-	-	-
23	21.3	21.3	81.1	76.2	BDL	0	19.3	-
24	-	-	64.9	64.9	-	-	-	-
25	-	-	100	72.3	-	-	-	-
26	-	-	90.9	73.9	-	-	-	-
27	-	-	-	-	-	-	-	-
28	19.4	14.8	87.6	84.6	72.7	3.1	44.3	26.7
29	-	-	-	-	-	-	-	-
30	27.8	18.7	BDL***	82.1	85.5	81.5	41.9	24.7
31	-	-	-	-	-	-	-	-
32	27.2	13.0	100	100	100	48.3	80.4	42.0
33	-	-	-	-	-	-	-	-
34	20.2	18.0	91.3	100	90.1	78.0	44.0	17.4
35	-	-	87.5	93.2	74.2	0	-	-

*** BDL = Below Detectable Limit

fermenter, but the solubilization of nickel was greater for the one-liter graduated cylinder (see lines 10 and 11 of Table 32).

Tests were conducted with the 14-liter fermenter to determine the effect of stirring speed on the degree of solubilization. Two samples of the same sludge were digested sequentially under identical conditions except that a stirring speed of 60 rpm was used for one sample and 600 rpm was used for the other. The results, shown in lines 13 and 14 of Table 32, indicate nearly identical solubilizations for the two samples. It is therefore concluded that the effect of stirring speed on solubilization is not significant.

The effect of the order in which acid and heat are applied to the sludge is shown by lines 16 and 17 of Table 32. Both cadmium and zinc were solubilized to a greater extent when the acid was added before heating (81% and 100%, respectively) rather than after heating (0% and 56%, respectively). This could be due in part to the longer exposure to acid when it is added before heating.

Comparison of lines 20 and 21 of Table 32 indicate a substantial increase in the amount of cadmium solubilized when the digestion time was increased from 30 to 60 minutes. A sample taken after 30 minutes of digestion indicated no cadmium solubilization while the sample taken after an additional 30-minute digestion of the same batch of sludge indicated 60% solubilization. In general, however, the digestion time was much less significant than this result would indicate.

The above results suggest that the conditions most conducive to heavy metals solubilization are:

--use of the 14-liter fermenter for digestion,
--use of 600 rpm stirring speed (primarily to promote good heat transfer and uniform conditions),
--acid addition before heating, and
--60 minutes digestion time.

These conditions were used in tests with sludges obtained from various municipal sources.

The test results of Table 32 indicate that the variable which exerts the greatest influence on metals solubilization is the amount of acid added. This is in agreement with the findings reported in Section 4. An attempt was made to correlate the degree of solubilization as a function of pH. The results for cadmium are shown in Figure 36. This correlation indicates a general trend toward higher solubilization of cadmium as the pH is decreased. At pH's greater than 2.5, there is essentially no solubilization of cadmium while at pH's below about 2.0, typically 80 to 100% of the cadmium is solubilized. Between pH 2 and 2.5, the data are widely scattered, ranging from zero to nearly 90%. These results are consistent with those presented in sections 4 and 5 for cadmium solubilization and in particular with the 0 to 90% solubilization range previously observed at pH 2.5.

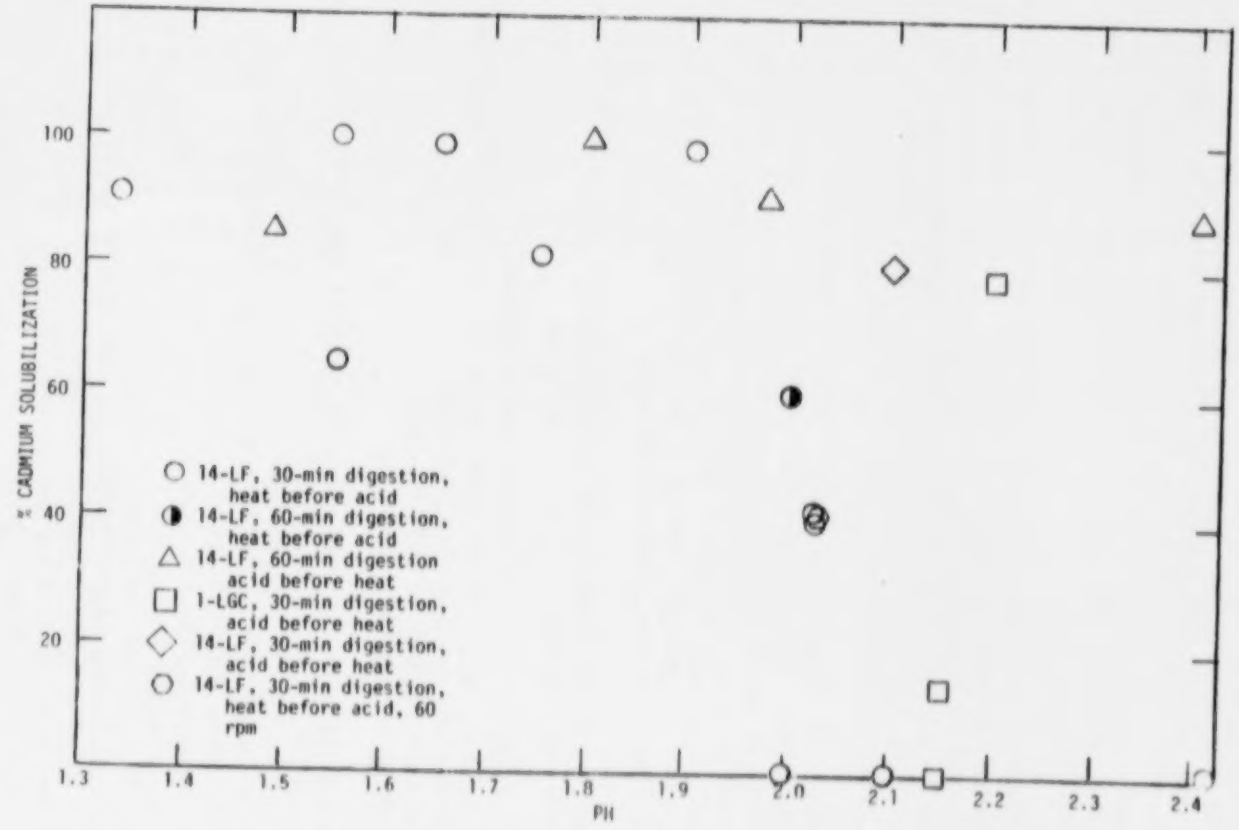


Figure 36. Cadmium solubilization as a function of pH.

A somewhat better correlation was obtained by plotting the degree of cadmium solubilization against the acid usage in kg of concentrated sulfuric acid (97%) per dry metric ton of solids. This plot is shown in Figure 37. Below an acid usage of about 125 kg/dmt there is no significant solubilization of cadmium, while above about 175 kg/dmt, 80 to 100% of the cadmium is solubilized. Thus the critical acid usage for good solubilization of cadmium is around 150 kg/dmt.

The fact that a better correlation was obtained on the basis of the amount of acid added rather than pH may indicate that the bulk pH of the sludge is not really representative of the hydrogen ion concentration at the reaction sites. This concept of a localized pH along with the steep slope of the curve in Figure 37 could explain the "erratic" solubilizations of cadmium noted in previous tests.

The solubilization of zinc as a function of acid usage is shown in Figure 38. The shape of the curve is similar to that for cadmium. The solubilization increases very rapidly over the range of 100 to 150 kg acid per dmt. Above this level the solubilization is generally in the range of 75 to 100%.

Results for nickel solubilization as a function of acid usage are shown in Figure 39. The degree of solubilization increases very sharply at about 125 kg/dmt. At higher acid usages the degree of solubilization varies between about 70 and 100%.

The results for chromium solubilization are shown in Figure 40. The degree of solubilization for chromium increases more gradually than for cadmium, zinc, and nickel and reaches a plateau of about 40% solubilized at higher acid usages.

In addition to heavy metals it is also of interest to know how the solubilization of solids and COD vary with acid usage. The plot for solubilization of solids is shown in Figure 41. The degree of solubilization appears to gradually increase up to an acid usage of about 150 kg/dmt but remains approximately constant thereafter at about 25%. The COD solubilization increased over the same range as shown in Figure 42. Above an acid usage of 150 kg/dmt the COD solubilization leveled off at 15-20%.

The results of Figures 37-40 indicate that good solubilization of the heavy metals can be obtained at acid usages of about 200 kg/dmt and above. This level was therefore specified for tests conducted with sludges obtained from various municipal sources. However, in order to add a fixed amount of acid per unit of solids, it is necessary to determine the solids content of the sludge prior to the test. The amount of acid to be added was calculated on the basis of the solids concentration as estimated by the various municipalities at the time the sludge was obtained. The actual solids content was not determined until after the tests were completed. Therefore, the acid usages for the sludges obtained from different cities varied from 225 to 325 kg/dmt.

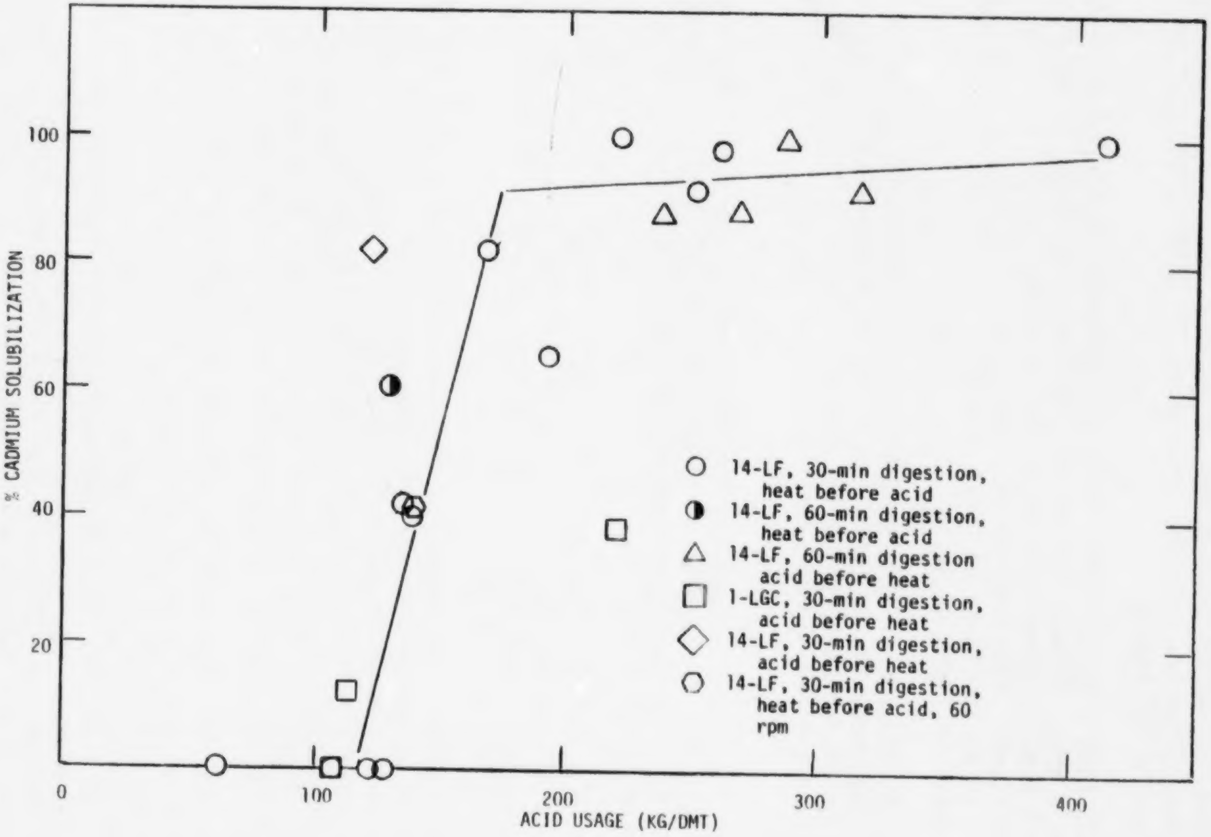


Figure 37. Cadmium solubilization as a function of acid usage.

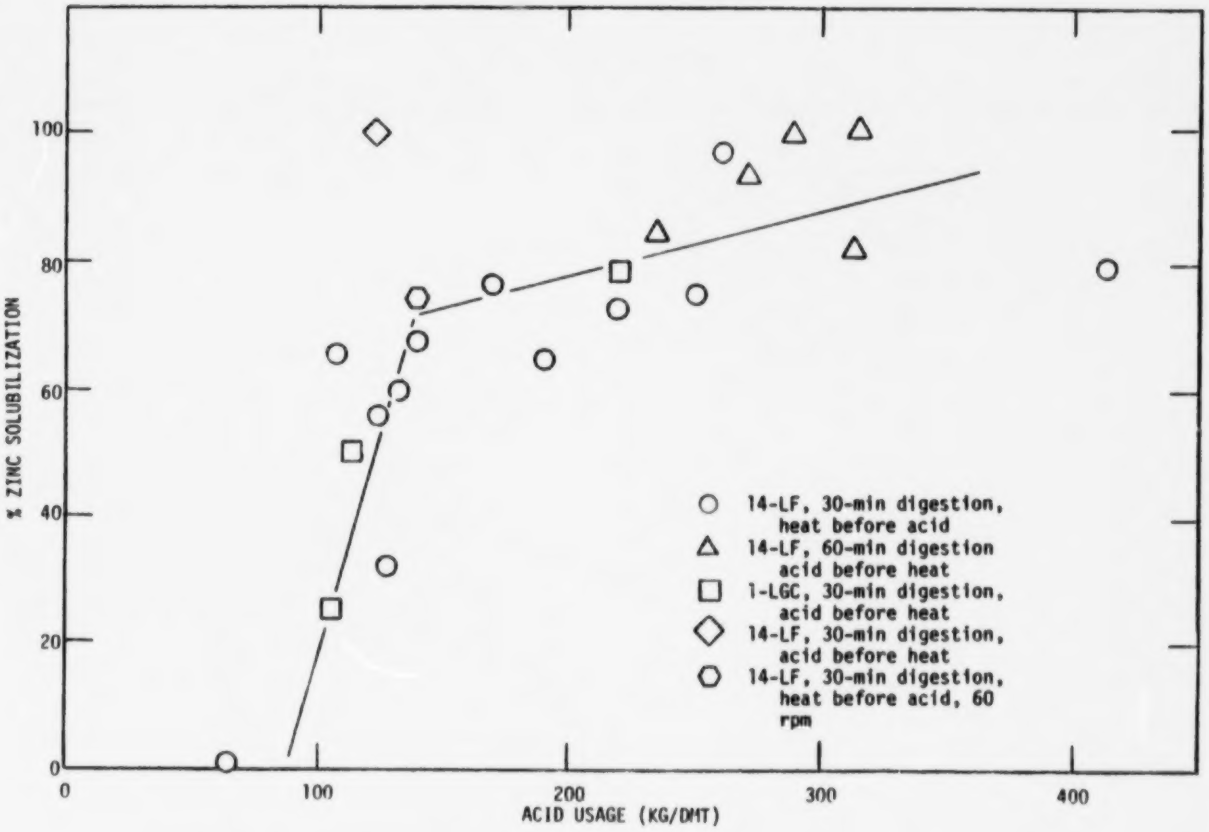


Figure 38. Zinc solubilization as a function of acid usage.

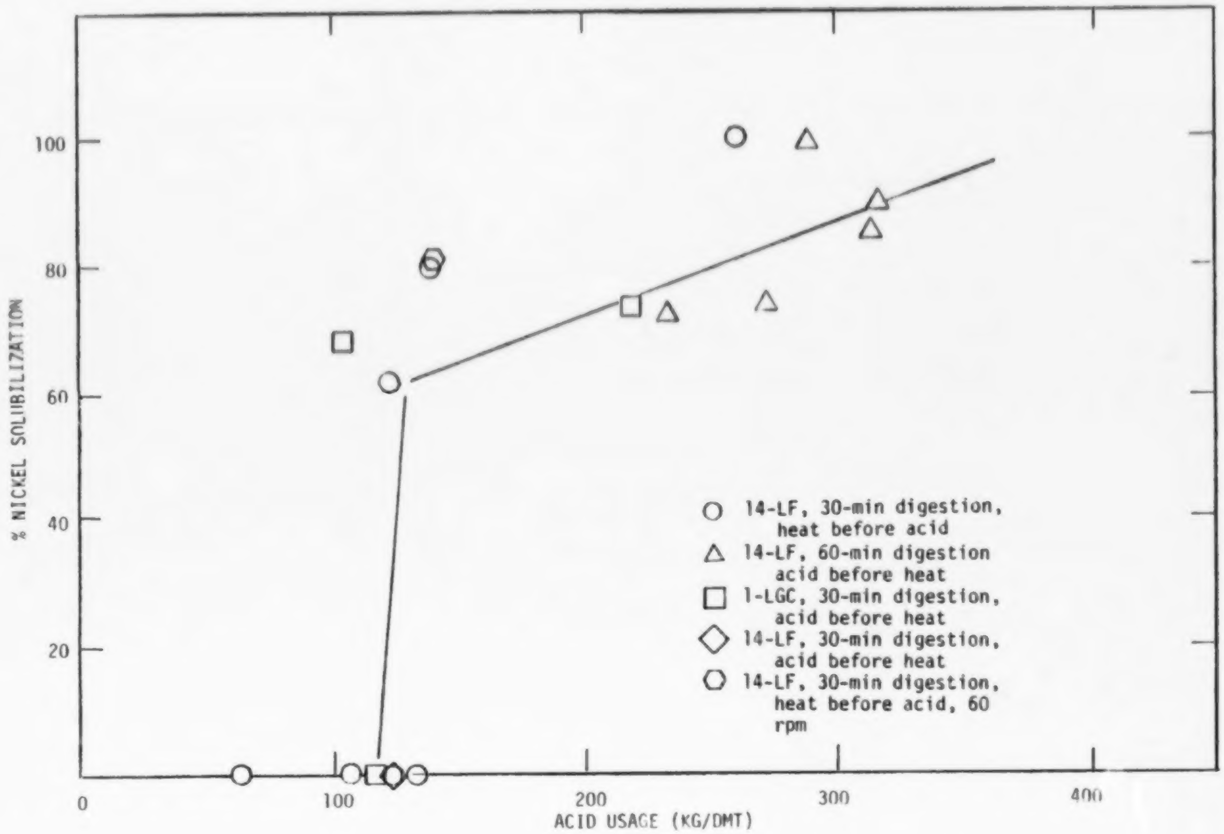


Figure 39. Nickel solubilization as a function of acid usage.

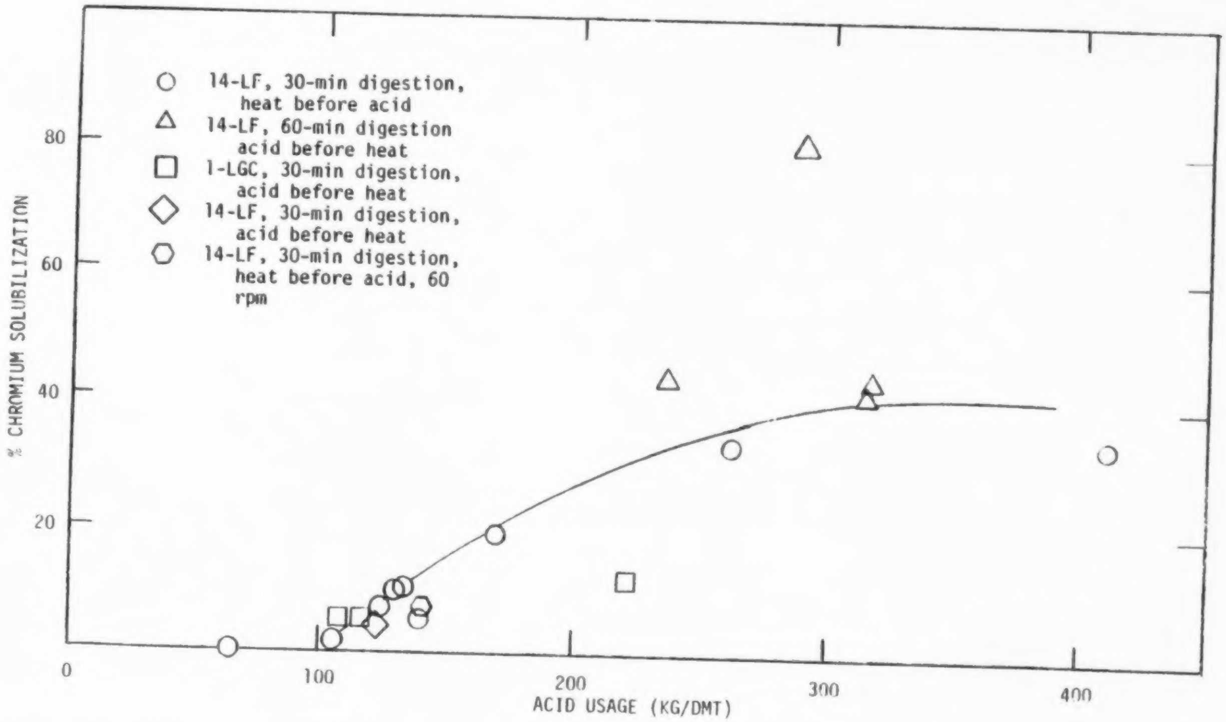


Figure 40. Chromium solubilization as a function of acid usage.

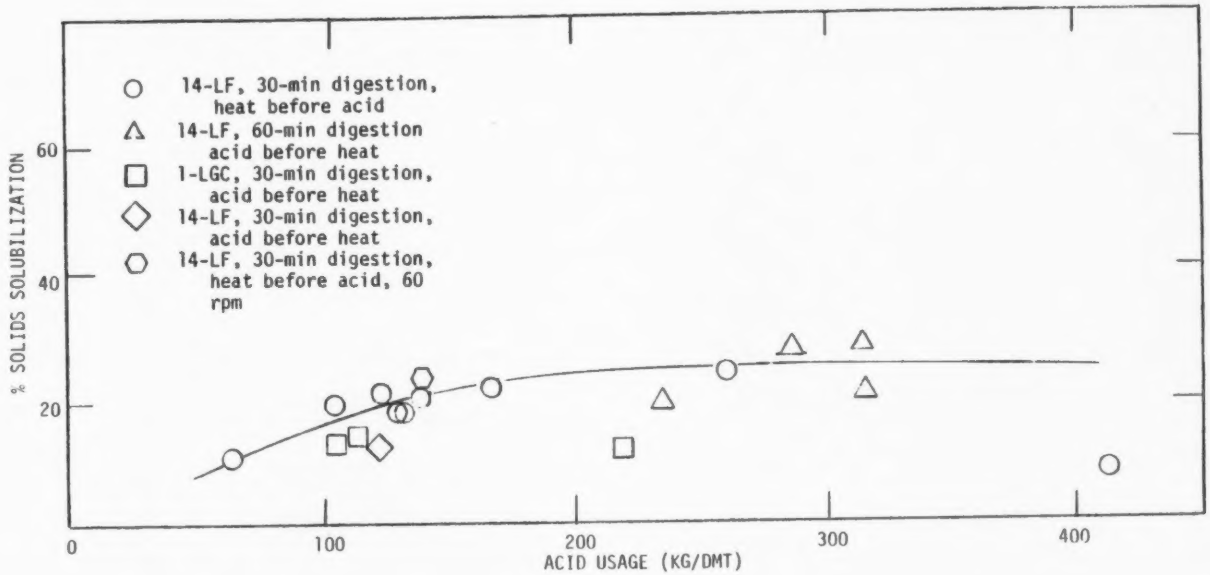


Figure 41. Solids solubilization as a function of acid usage.

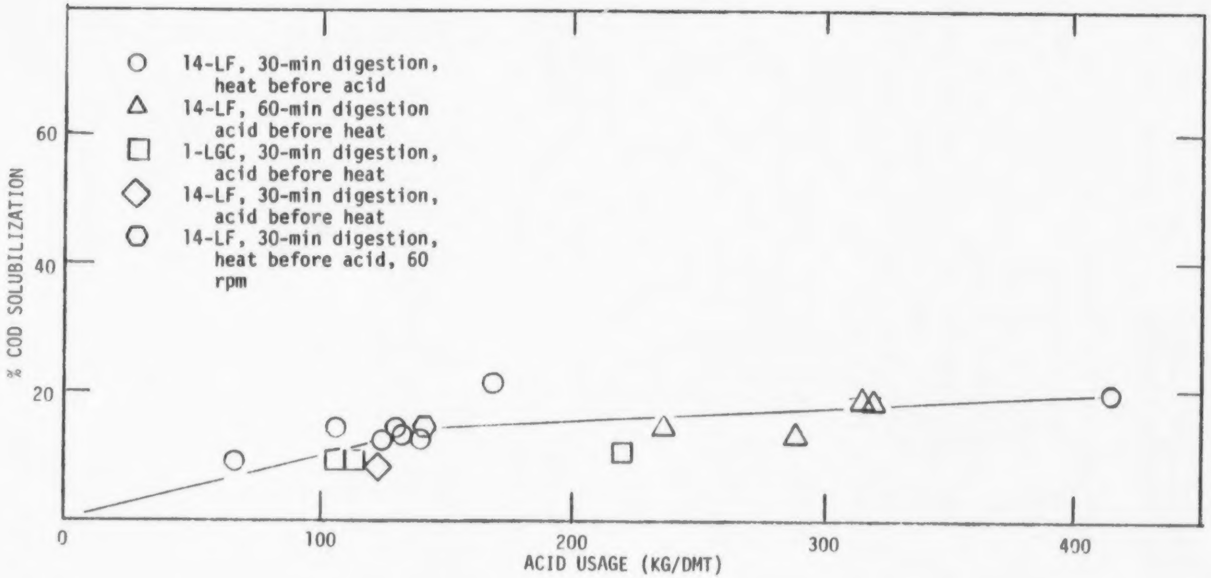


Figure 42. COD solubilization as a function of acid usage.

Table 32 (lines 27-35) shows the degree of solubilization for various sludge constituents as a function of acid usage at the preferred operating conditions (14-liter fermenter, 600 rpm, acid addition before heating, 60 minute digestion time, and acid usage > 200 kg/dmt). Tests were conducted with samples of sludge from Brockton, MA, Fitchburg, MA, Lawrence, MA, and Milwaukee, WI (two tests on same sample). The mean solubilizations and ranges obtained for the various sludges are given in Table 33.

Excellent solubilizations were obtained for cadmium, zinc, and nickel and moderate solubilizations were obtained for chromium and copper. With the exception of copper the range of solubilizations of heavy metals was reasonably narrow indicating that at an acid usage of >200 kg/dmt the solubilization curve has reached its plateau. For copper, the results of Table 32 (lines 27-35) indicate that the solubilization increases from zero to 80% over a range of acid usage of 270 - 315 kg/dmt. Thus copper is more difficult to solubilize than other heavy metals and requires an acid usage of >300 kg/dmt for good solubilization.

Reasonably good agreement (except for copper as noted above) was obtained for solubilization of a given constituent from the various sludges as shown by the range of solubilizations in Table 33. The sample of Lawrence, MA sludge exhibited the best solubilizations of heavy metals (100% for cadmium, zinc, and nickel; 80% for chromium) but also exhibited the highest solubilization of nitrogen (42%). This may indicate that a significantly lower acid usage could be applied to the Lawrence sludge to achieve acceptable solubilizations. In general, however, the results indicate that the acid usage criteria of >200 kg/dmt for solubilization of cadmium, zinc, nickel, and chrome, and >300 kg/dmt for solubilization of copper are applicable to sludges from various municipalities

It is of interest to compare the costs of the hot acid process optimized for heavy metals removal to the same process optimized for dewatering. The major difference in operating cost will result from differences in acid usages for the two cases. Based on the results of Section 4, optimum dewatering is obtained at a digestion pH of about 2.5. From Figure 12, the acid requirement to achieve a pH of 2.5 ranges from 70 to 100 kg/dmt. For optimum metals removal (except copper) the acid requirement is approximately 200 kg/dmt which is a factor of two to three times greater than for optimum dewatering.

Based on an acid cost of $49.50 per metric ton ($45 per short ton) for concentrated sulfuric acid, the costs per ton of solids treated are:

Process	Acid usage kg/dmt	Acid cost $/dmt	Acid cost $/dst
Optimized for Dewatering	100	4.95	4.50
Optimized for Metals Removal	200	9.90	9.00

TABLE 33. SOLUBILIZATIONS OBTAINED FOR SLUDGES FROM VARIOUS CITIES AT PREFERRED OPERATING CONDITIONS

Sludge constituent	Mean solubilization %	Range of solubilizations %
Cadmium	92	88 - 100
Zinc	92	82 - 100
Nickel	84	73 - 100
Chromium	53	42 - 80
Copper	53	3 - 82
Solids	24	19 - 28
Organics (COD)	16	13 - 19
Nitrogen (TKN)	28	17 - 42

Thus, for the hot acid process, the cost differential for acidification between optimized dewatering and optimized metals removal is only about $5/dmt which is considered to be quite reasonable.

CONCLUSIONS

Additional bench-scale tests were conducted to define the factors responsible for solubilization of heavy metals and to optimize the hot acid process for heavy metals removal. Consistent correlations were obtained between the degree of solubilization and the acid usage in kg of concentrated H_2SO_4 per dmt. These correlations indicate a rapid increase in the degree of solubilization of cadmium, zinc, nickel, and chromium over the range of 100 to 200 kg/dmt and of copper (based on limited data) over the range of 250 to 300 kg/dmt. The correlation of metals solubilization with "acid usage" was found to be more consistent than correlation with "pH".

Tests conducted with fresh WAS samples from various municipalities indicated excellent solubilization of cadmium (88-100%), zinc (82-100%), and nickel (73-100%) at acid usages >200 kg/dmt. Only moderate solubilization of chromium (∿45%) was obtained, and appreciable copper solubilization (∿80%) required a higher acid usage (>300 kg/dmt). For these tests, average solids, COD, and TKN solubilizations were 24, 16, and 28%, respectively.

An acid usage of 200 kg/dmt was selected as the optimum for heavy metals solubilization. This is two to three times as great as the acid usage required for optimum dewatering (70-100 kg/dmt to achieve pH 2.5). However, the cost for acid at a usage of 200 kg/dmt is still <$10/dmt ($9/dst) and is considered to be quite acceptable for the levels of solubilization obtained.

SECTION 7

SPECIFICATION OF SOLIDS - SEPARATION EQUIPMENT

Three techniques for solid-liquid separation: settling, vacuum filtration, and centrifugation were investigated during bench-scale tests. The solid-liquid separation tests were conducted for the purpose of identifying the effects of changes in the process variables on solids separation rates and were not intended for generation of design data for full-scale dewatering equipment. The rationale for concluding that the hot acid process produces a sludge with adequate dewatering characteristics is based on:

1) the substantial improvement in dewatering characteristics relative to the untreated sludge, and

2) the results of Figures 33 and 34 which indicate that filtration and centrifugation rates are as favorable as for chemically conditioned sludge.

Of the three solid-liquid separation techniques evaluated, settling appeared to have the least potential applicability to the hot acid treatment process. Thickening of the sludge prior to hot acid treatment is very important in reducing the treatment costs. However, for properly thickened sludge, the hot acid process does not produce rapid additional settling. As shown in Figure 14, the volume of treated sludge was reduced by only about 10% during 30 minutes of settling following hot acid treatment. The rate and extent of settling observed during the bench-scale tests appeared inadequate to justify the added cost and complexity of settling before final dewatering of the sludge.

The bench-scale filtration data can be analyzed to give the specific resistance of the filter cake which can then be used to calculate the filter yield(8). The specific resistance for raw Brockton WAS (see filtration curve of Figure 33) was approximately 1.5×10^{10} sec^2/g. The hot acid process (or chemical conditioning) reduced the specific resistance to approximately 1.5×10^9 sec^2/g. This resistance is higher than the level at which good filtration results are normally obtained (10^8 sec^2/g (15)).

A number of attempts were made to obtain filtration data using a filter leaf apparatus. However none of the filter materials tried gave satisfactory results: some filter materials plugged allowing no passage of filtrate while others permitted near complete passage of both solids and liquid. Consequently the filter leaf tests were abandoned.

Of the solid-liquid separation techniques evaluated, centrifugation was selected as the preferred technique for sludge dewatering following hot acid treatment. This selection was based on several considerations:

1. The centrifugation curve for hot acid treatment (see Figure 34) fell approximately mid-way between the curves for chemical treatment and thermal treatment. This was taken as an indication that centrifugation rather than filtration was better suited for dewatering the hot-acid-treated sludge.

2. The high specific resistance and problems with the filter leaf test indicated potential problems for dewatering by vacuum filtration.

3. In the initial process design, the digested sludge was dewatered before cooling (by heat exchange with the feed) in order to take advantage of the lower viscosity of water at elevated temperatures. Vacuum filtration was not considered well-suited for dewatering hot sludge because of potential odor problems and potential heat loss from the filtrate by vacuum evaporation. (However, this process design was later abandoned when economic calculations indicated a large energy-cost penalty associated with failure to recover heat from the sludge solids.)

4. Centrifugation appeared to have certain other advantages over vacuum filtration such as lower costs and operating labor (8).

Based on these advantages bench-scale and pilot-scale centrifugation tests were conducted at Bird Machine Co., South Walpole, MA. The test results are given in Appendix B. On the basis of the bench-scale tests it was concluded that hot-acid-treated sludge would be a good application for a continuous solid bowl centrifuge, and pilot-scale tests were recommended. However, during the bench-scale tests, lime, ferric chloride, and various polymers were used to improve the solid-liquid separation. Because of the cost of these additives and their potential for adsorption or precipitation of solubilized heavy metals, the pilot-scale tests were conducted without chemical additives. For these tests good cake solids concentrations (18-36% solids) were obtained, but solids recoveries were low. The use of flocculents was recommended to improve the recovery of solids as cake. Based on these tests, the full-scale dewatering equipment specified by Bird Machine Co. for hot-acid-treated Brockton WAS is shown in Table 34.

While centrifugation can be used to dewater hot-acid-treated sludge, other solid-liquid separation devices may offer significant advantages over centrifugation and should be evaluated. Of particular interest is the filter belt press which can generally produce higher cake consistencies than centrifugation and operate with significantly lower power and maintenance requirements (19).

TABLE 34. SPECIFICATION FOR CENTRIFUGES TO DEWATER BROCKTON WAS FOLLOWING HOT ACID TREATMENT

Centrifuge Capacity				
Solids		Liquid		
kg/hr	(lb/hr)	lpm	(gpm)	Description*
68	(150)	38	(10)	One Bird Machine Co. HB1400 or equivalent
680	(1,500)	380	(100)	One Bird Machine Co. HB3700 or equivalent
6,800	(15,000)	3,800	(1,000)	Three Bird Machine Co. HB64000 or equivalent

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* All machines are horizontal, solid-bowl, conveyor-type centrifuges. Materials of construction are 300-series stainless steel. Centrifuges are of the low-speed, sludge-dewatering type which operate in the range of 500-800 x gravity.

SECTION 8

SPECIFICATIONS FOR PILOT SYSTEM

The process flow schematic for a 5 gpm, pilot-scale, hot-acid-treatment system is shown in Figure 43. Primary sludge (which has been screened to remove gross particulates) and waste activated sludge are mixed in the desired proportions and pass through in float control valve that maintains a constant level in the feed tank. The feed tank is agitated by a 0.19kw (0.25 h.p.) mixer to insure complete mixing of the two sludges, and the 10 minutes residence time in the 0.2 m^3 (50 gal) tank smoothes any sudden changes in feed composition.

A progressive cavity pump circulates sludge through the pilot plant. This type of pump provides a constant flow rate with varying upstream pressure and can pump abrasive solids and viscous sludges. The flow rate is controlled by varying the quantity of sludge returned to the pump suction through the bypass valve. The ultrasonic flow meter and total flow counter, which uses the Doppler principle to measure velocity, is attached to the outside wall of the pipe and does not contact the sludge.

The sludge is heated in two stages. In the first stage, the feed sludge is heated to approximately (75°C) by exchange with the hot digested sludge; in the second stage steam heats the sludge to the desired digestion temperature (90-95°C). A co-axial double pipe heat exchanger is used for the first stage since both sludge and concentrate contain solids which may settle out unless a high velocity is maintained in both streams. A shell and tube heat exchanger with an area of 2.5 m^2 (27 ft^2) (based on an estimated overall heat transfer coefficient, U, of 270 W/m^2 °C (50 Btu/hr-ft^2-°F) is used in the second stage with the sludge on the tube side to avoid settling. A 68 kW boiler, capable of generating 95 kg steam/hour (210 lb steam/hour), supplies steam to the second stage at 450 kN/m^2 (50 psig), and the rate of steam supply is controlled by a temperature controller.

The pH of the feed is adjusted to the desired level (pH 2-3) in a 0.1 m^3 (25 gal) mixing tank by adding concentrated sulfuric acid at a rate of approximately 0.1 kg acid/kg sludge solids (2 l/hr of 95% acid for sludge with 3% solids). A pH probe with a feedback control system regulates the acid metering pump. The pH is adjusted after the heat exchanger rather than before in order to reduce corrosion and recover heat from the solids stream.

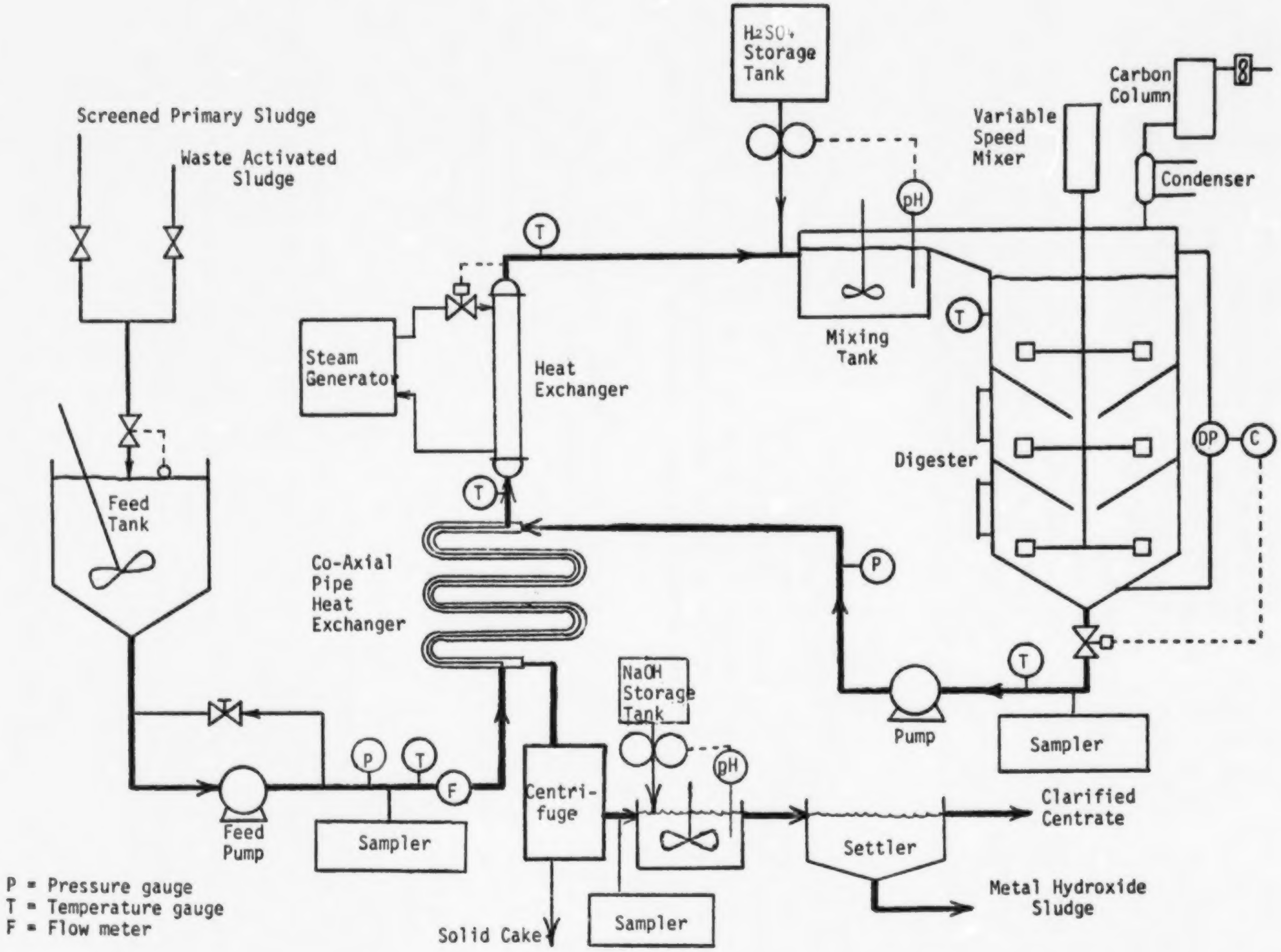
Screened Primary Sludge
Waste Activated Sludge
Feed Tank
Feed Pump
Sampler
P
T
F
Steam Generator
Heat Exchanger
T
T
Co-Axial Pipe Heat Exchanger
Centri-fuge
Solid Cake
NaOH Storage Tank
pH
Sampler
Settler
Clarified Centrate
Metal Hydroxide Sludge
H2SO4 Storage Tank
pH
Mixing Tank
T
Variable Speed Mixer
Carbon Column
Condenser
Digester
DP
C
P
T
Pump
Sampler
P = Pressure gauge
T = Temperature gauge
F = Flow meter

Figure 43. Process flow schematic for 5 gpm hot acid treatment pilot plant.

The hot acidified feed flows from the mixing tank over a weir to the digester where it is held for the desired residence time. The digester has a total volume of 0.57 m^3 (150 gallons) to provide a maximum residence time of 30 minutes at the design flow rate of 19 l/min (5 gpm). The tank is constructed of fiberglass with a 30°-slope conical bottom, a height of 2 m, and a diameter of 0.65 m. The volume is divided into three equal stages by two 30° conical baffles with 10-cm-diameter holes in the center of each. This configuration reduces axial mixing which for an unbaffled tank would result in a poor residence time distribution.

A variable speed mixer (20-350 rpm) with a turbine agitator in each stage can be used to determine the effect of agitation on performance. The mixer has an independent support structure to avoid stresses in the fiberglass digester tank. A manhole in each digester section allows assembly of the agitators to the mixer shaft and cleaning between the baffles (should this be necessary).

The level (residence time) in the digester is maintained by a differential pressure level transducer and controller that maintains a constant preset pressure differential across the sludge by adjusting a proportional flow control valve at the bottom of the digester. A small air blower maintains a slightly reduced pressure in the digester and pH mixing tank to avoid venting untreated gases past the agitator shaft and unsealed tank connections. The gases from the blower are vented through a condenser and carbon adsorption column.

Following cooling (heat recovery) in the first stage heat exchanger, the treated sludge is centrifuged to remove solids. (Other dewatering devices could also be evaluated). The solid cake is discharged; and the concentrate flows into a 0.075 m^3 (20 gallon) surge tank where the pH is adjusted by the addition of sodium hydroxide (NaOH) or lime to precipitate heavy metals. The pH can be varied to determine the optimum level for maximum metals removal. The precipitated metals are settled in a clarifier with a surface area of approximately 0.7 m^2 (7 ft^2). It is anticipated that other suspended solids will coagulate and settle with the metal hydroxides. The clarified overflow is pumped back to the secondary treatment system. Batch tests can be conducted to evaluate various dewatering techniques for the settled heavy metal sludge, but it is anticipated that the flow of sludge will be too small to allow continuous dewatering.

Temperature (T) and pressure (P) are monitored at strategic locations as indicated in Figure 43. Automatic vacuum lift samplers are used to obtain samples of untreated sludge, dewatered sludge, and centrate. Either time-averaged composites or sequential samples can be collected.

Specifications and approximate costs of the equipment required to build the pilot plant are shown in Table 35. The approximate total purchased equipment cost, not including sludge dewatering, is $40,000. To this cost must be added the cost of sludge dewatering equipment, the cost of system design and engineering, and the cost of site preparation and installation.

TABLE 35. SPECIFICATION OF PILOT SYSTEM COMPONENTS

Item		Description	Approximate Cost
1	Float Control Valve	3/4 NPT Polypropylene	115
2	Feed Tank	25 Gallon capacity, conical bottom Polypropylene	160
3	Feed Tank Stirrer	1/4 h.p., 350 r.p.m. stainless steel shaft and impeller.	450
4	Feed Pump	Progressive cavity type; 5 gpm at 60 psi, 3/4 h.p. motor;	1200
5	Flow Meter	Ultrasonic with total flow counter non-contacting 0-10 gpm	2450
6	Heat exchanger (Stage 1)	Co-axial double pipe type sludge inside-pipe, centrate outside-pipe All stainless steel	800
7	Heat exchanger (Stage 2)	Shell and tube type sludge tubeside, steam shellside 28 ft^2 of tube area Admirally tubes.	1350
8	Steam generator	Self contained with feedwater treatment 200 lb steam/hour (approx 70kw)	2100
9	Steam control valve	Temperature Regulated with internal Pilot Operating range 150-220°F	285
10	Acid mixing tank	25 gallon capacity, polypropylene	105

(Continued)

TABLE 35 (CONTINUED)

	Item	Description	Approximate Cost
11	pH control system	Automatic temperature compensating electrodes Indicator/controller regulating variable speed flexible tubing pump.	1100
12	Mixer	3 1/4 h.p., 350 r.p.m. stainless steel shaft and impeller.	450
13	Acid storage tank	200 gallon stainless steel tank	650
14	Digester Tank	150 gallon capacity, conical bottom with two conical baffles Manholes for access to lower two compartments fiberglass construction	
15	Agitator	Variable speed drive 350-20 r.p.m. 0.75h.p. stainless steel shaft and turbines.	1600
16	Level Controller	Differential pressure transducer and controller regulating digester outlet valve	1660
17	Digester Vent	5 SCFM air blower Condenser and Carbon Adsorber	735
18	Surge Tank	25 gallon Polypropylene	100
19	Pump	Centrifugal, 5 gpm at 20 psi	435
20	Float Control Valve	1/2 NPT Polypropylene	90
21	Caustic Mixing Tank	20 gallon Polypropylene	80
22	pH Control System	Automatic temperature compensating electrodes Indicator/controller regulating variable speed flexible tubing pump	1100

(Continued)

TABLE 35 (CONTINUED)

	Item	Description	Approximate Cost
23	Mixer	3 1/4 h.p., 350 r.p.m. Stainless steel shaft and impeller	450
24	Caustic Storage Tank	200 gallon Stainless Steel Tank	650
25	Flocculator Clarifier	7 ft^2 Surface Area	9000
26	Sampler	Vacuum Lift Type Stainless Steel Components Refrigerated Storage of Samples	2600

SECTION 9

ENERGY AND ECONOMIC ANALYSES

A simplified flow schematic of the hot acid sludge conditioning system is shown in Figure 44. Thickened sludge is pumped through a heat exchanger in which the sludge temperature is increased by heat recovered from the treated sludge. The sludge is then acidified with concentrated sulfuric acid (H_2SO_4) in a flash mixing tank before entering the digester. In the digester the sludge is brought to digestion temperature by steam circulated through heating coils and is retained for the desired residence time.

After digestion the sludge is pumped back through the heat exchanger (for energy recovery) to the centrifuge where the sludge is dewatered. Because of the low pH, it may be necessary to neutralize the solid cake prior to land application. This can be accomplished by the addition of anhydrous ammonia which will also increase the nitrogen value of the sludge. The liquid concentrate is returned to the secondary treatment system after pH adjustment and settling to precipitate heavy metal hydroxides.

Cost estimates have been developed for hot acid sludge conditioning systems to treat 200, 20 and 2 dmtpd (dry metric tons per day) of sludge solids. These are the approximate quantities of primary plus waste activated sludge generated by wastewater treatment plants of 500, 50, and 5 m^3/min (200, 20 and 2 million gallons per day) capacity, respectively (20). The assumptions and design bases used to develop the cost estimates are given in Table 36.

The flow rates of the various streams in the system are shown in Figure 45. It is assumed that the sludge is thickened to 3% solids prior to conditioning, and after conditioning the centrifuge produces a sludge cake with 20% solids. From Figure 12 the acid demand is taken as 0.1 kg H_2SO_4 per kg of sludge solids which should reduce the pH to 2.0 - 2.5. As pointed out in Section 6, optimum metals removal would require about twice this amount of acid.

The energy balance around the system is shown in Figure 46. The thickened sludge is initially heated to 80°C in the heat exchanger by energy recovered from the treated sludge (approximately 80% of the heat is recovered). The sludge is further heated to 95°C in the digester by steam passed through the heating coils. Following digestion, during which heat losses are assumed to be negligible, the temperature is reduced to 35°C in the

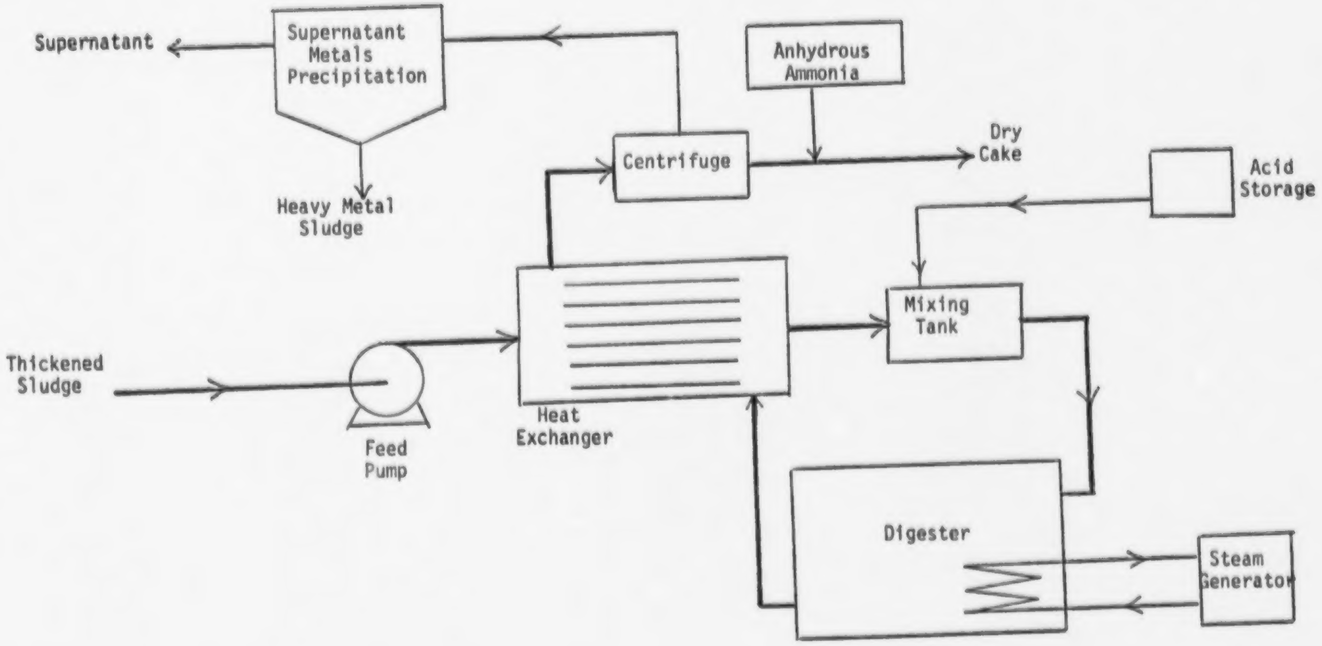
Supernatant
Supernatant Metals Precipitation
Heavy Metal Sludge
Anhydrous Ammonia
Centrifuge
Dry Cake
Acid Storage
Thickened Sludge
Feed Pump
Heat Exchanger
Mixing Tank
Digester
Steam Generator

Figure 44. Simplified flow schematic of hot acid sludge treatment process.

TABLE 36. ASSUMPTIONS AND DESIGN BASES FOR ECONOMIC ANALYSIS

Sludge solids treated, dmtpd	2	20	200
Feed sludge solids concentration, percent	3	3	3
Feed sludge flow rate, m^3/hr (gpm)	2.8(12.2)	28(122)	280(1220)
Feed sludge temperature: Entering H/E, °C	20	20	20
Leaving H/E, °C	80	80	80
Treated sludge temperature: Entering H/E, °C	95	95	95
Leaving H/E, °C	35	35	35
Overall coefficient of heat transfer for H/E, W/m^2 °C (Btu/hr ft^2 °F)	575(100)	575(100)	575(100)
Surface area of heat exchanger, m^2 (ft^2)	23(250)	230(2,500)	2300(25,000)
Digestion pH	2.0	2.0	2.0
Sludge acid demand, kg acid/kg sludge solids	0.1	0.1	0.1
Acid flow rate, kg/hr	8.3	83	830
Acid price, 66°Be H_2SO_4, \$/kg (\$/short ton)(a)	0.05(45)	0.05(45)	0.05(45)
Acid cost, \$/hr	0.415	4.15	41.5
Overall coefficient of heat transfer of coils in digester, W/m^2 °C(Btu/hr ft^2 °F)	575(100)	575(100)	575(100)
Sludge temperature in digester, °C	95	95	95
Steam pressure, kN/m^2 (psig)	450(50)	450(50)	450(50)
Steam flow rate to digester, kg/hr (lb/hr)	82.5(182)	825(1820)	8250(18,200)
Energy to generate steam, kW	48.5	485	4850
Cost of No. 4 fuel oil, \$/kW-hr (b)	0.009	0.009	0.009
Sludge residence time in digester, min	30	30	30
Total pump head, m	30	30	30
Pump efficiency, %	70	70	70
Miscellaneous electric power, kW	2	12	72
Electric power cost, \$/kW-hr(b)	0.05	0.05	0.05
Labor man-days/year (conditioning)	200	275	360
Labor rate \$/man-day (incl. fringe benefits)	100	100	100
Annual capital cost (20-year life, 7% per annum interest) as % of capital investment	9.4	9.4	9.4
Maintenance materials, % of total O&M cost	5	5	5

(continued)

TABLE 36. CONTINUED

Sludge solids treated, dmtpd	2	20	200
Centrifuge power, kW[(b)]	11	30	246
Additional labor for centrifuge, man-day/year	20	25	40
Lime demand, kg lime/m^3 supernatant[(c)]	3	3	3
Lime flow rate kg/hr	7.2	72	720
Lime cost, \$/kg (\$/100 lbs)[(d)]	0.0325(1.50)	0.0325(1.50)	0.0325(1.50)

(a) Quotation, May 1978.

(b) Private communication with supplier.

(c) Based on experimental dosage required to raise pH from 1.85 to 9.0.

(d) Reference 12

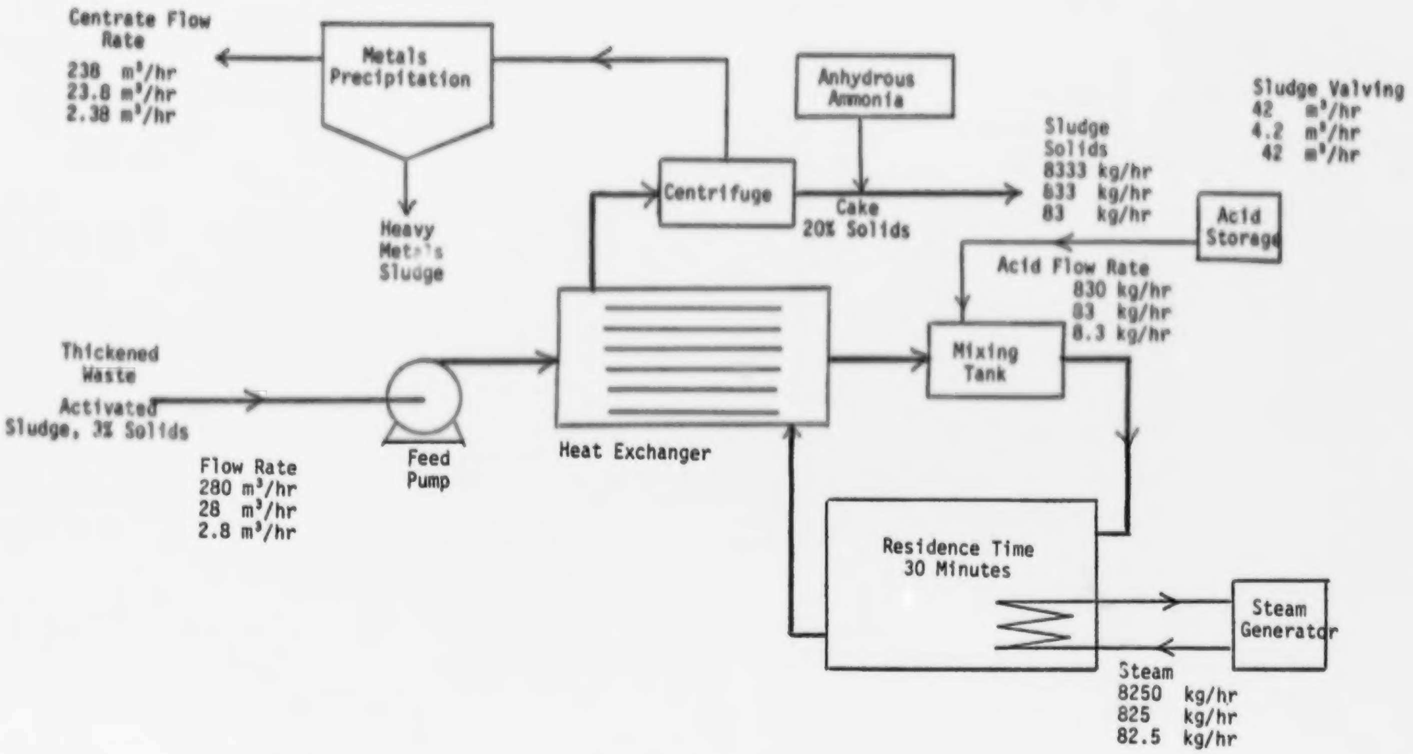
Centrate Flow Rate
238 m^3/hr
23.8 m^3/hr
2.38 m^3/hr
Metals Precipitation
Heavy Metals Sludge
Anhydrous Ammonia
Centrifuge
Cake 20% Solids
Sludge Solids
8333 kg/hr
833 kg/hr
83 kg/hr
Sludge Valving
42 m^3/hr
4.2 m^3/hr
42 m^3/hr
Acid Storage
Acid Flow Rate
830 kg/hr
83 kg/hr
8.3 kg/hr
Thickened Waste Activated Sludge, 3% Solids
Flow Rate
280 m^3/hr
28 m^3/hr
2.8 m^3/hr
Feed Pump
Heat Exchanger
Mixing Tank
Residence Time 30 Minutes
Steam Generator
Steam
8250 kg/hr
825 kg/hr
82.5 kg/hr

Figure 45. Material balance results for full-scale hot acid treatment system.

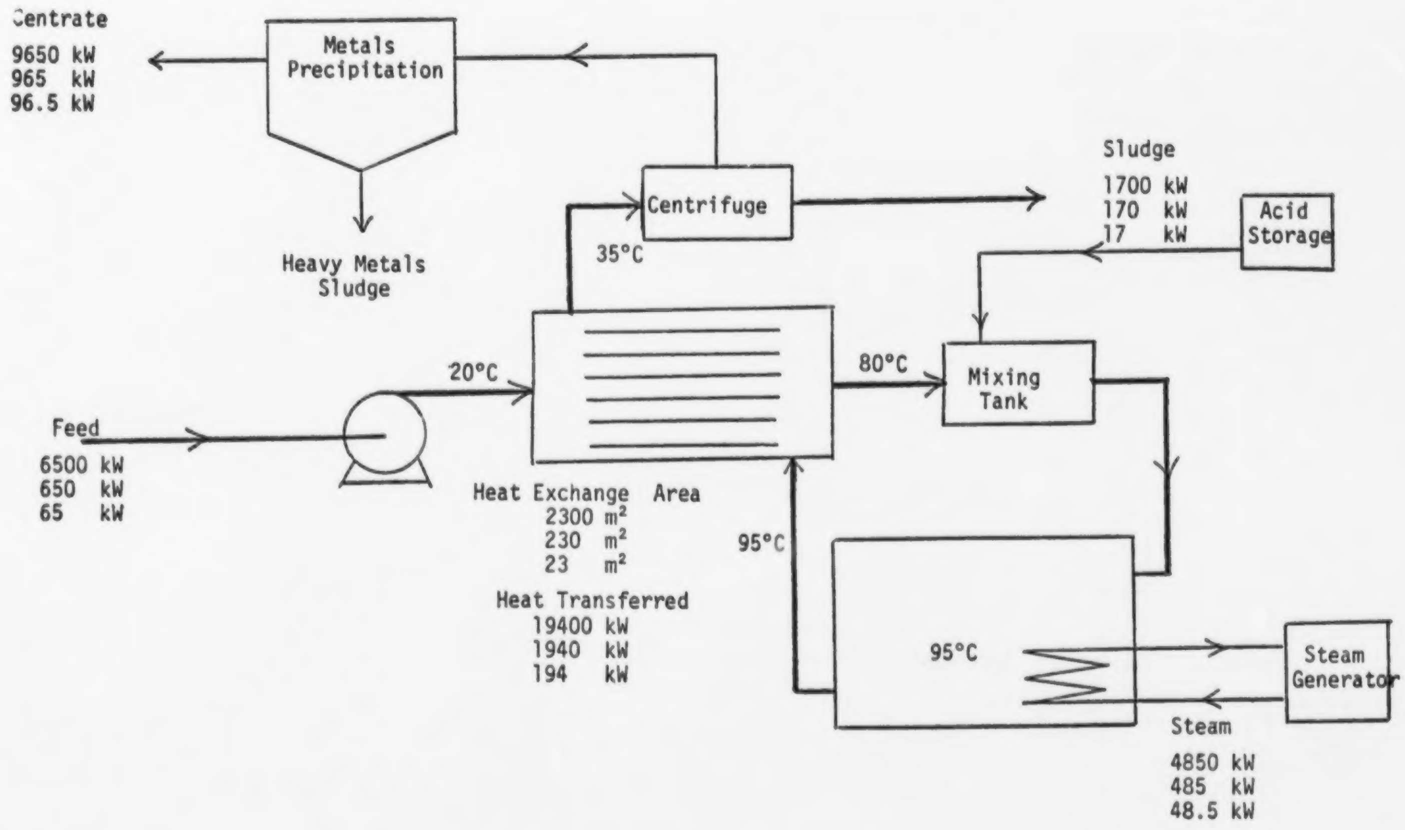
Centrate
9650 kW
965 kW
96.5 kW
Metals Precipitation
Heavy Metals Sludge
Centrifuge
Sludge
1700 kW
170 kW
17 kW
Acid Storage
35°C
20°C
80°C
Mixing Tank
Feed
6500 kW
650 kW
65 kW
Heat Exchange Area
2300 m²
230 m²
23 m²
Heat Transferred
19400 kW
1940 kW
194 kW
95°C
95°C
Steam Generator
Steam
4850 kW
485 kW
48.5 kW

Figure 46. Energy balance results for full-scale hot acid treatment system.

heat exchanger before entering the centrifuge. The sludge is dewatered after, rather than before, heat recovery so that heat can be recovered from the sludge solids. The lower sludge temperature in the centrifuge increases viscosity and hence the required centrifuge capacity; however, the additional heat recovered more than compensates for the added centrifugation costs.

Cost estimates or quotations for all major pieces of process equipment are given in Table 37. All costs are adjusted to an EPA - Sewage Treatment Plant Construction Cost Index (EPA-STPCCI) of 288 (fourth quarter 1977). Land costs are not included since these costs are site specific, and in an integrated plant it is difficult to segregate the component of land cost attributable to sludge conditioning from that attributable to other wastewater and sludge treatment processes.

Capital costs are shown in Table 38. Equipment installation is estimated to cost 40% of the purchased equipment cost. Installation is defined as site preparation (assuming reasonable subsoil conditions), foundations, and transportation and positioning of equipment. It does not include equipment hook-up which is included with piping, electrical and instrumentation. Engineering, legal and contingency is estimated at 37.5% of the total plant cost (21) and includes all costs not directly attributable to materials and labor for plant construction, such as construction financing, contractor fees, construction management, etc. These cost factors are obviously generalizations of costs which will vary with local conditions. The overall capital investment computed using these factors is approximately 2.4 times the purchased equipment cost, which is in close agreement with other estimates given in the literature (21,22).

The capital costs are shown for both the hot acid treatment process alone, and hot acid treatment in conjunction with centrifugal dewatering and supernatant treatment. In this way, costs can be compared directly either with other conditioning techniques or with complete conditioning and dewatering systems.

Operating and maintenance cost estimates are shown in Table 39. It is assumed that energy to heat the sludge is provided by No. 4 fuel oil at a cost of $0.009/kWhr, and that all other power would be electrical at a cost of $0.05/kWhr. Operating labor was estimated assuming a fully automatic system requiring only periodic routine checks. The labor rate was estimated at $100 per man-day and includes all salary related costs and supervision. No attempt is made to differentiate between operating and maintenance labor.

The capital-recovery-factor method (23) was used to determine investor capitalization. In essence, this technique calculates the equal annual payment which must be made to yield the same sum at the end of the plant life as if the capital had been invested at compound interest when the plant was constructed. It is assumed that the plant has a 20 year life with no resale value, and the annual interest rate is 7%. Under these circumstances the yearly cost of financing the construction is equal to 9.4% of the total fixed capital investment.

TABLE 37. PURCHASED EQUIPMENT COST FOR HOT ACID TREATMENT

Plant size, dmtpd	2	20	200
Sludge pumps, \$	2,200	6,300	11,300
Heat exchanger, \$	8,800	50,500	310,000
Acidification, \$	7,500	17,500	44,000
Digester[(a)], \$	4,300	16,000	111,000
Steam generator, \$	3,000	13,000	100,000
Total purchased equipment cost (PEC) for hot acid treatment, \$	25,800	103,300	576,300
Centrifuge, \$	75,000	110,000	945,000
Supernatant treatment system, \$	13,000	67,000	160,000[(b)]
Total purchased equipment cost (PEC) for sludge conditioning, dewatering, and supernatant treatment, \$	113,800	280,300	1,681,300

Note: All capital cost estimates obtained from vendors, except as noted below:

(a) Vendors literature
(b) Reference 15. Costs adjusted to EPA-STPCCI 288.

TABLE 38. CAPITAL COSTS FOR HOT ACID TREATMENT

Plant size, dmtpd	2	20	200
CASE I: HOT ACID TREATMENT ONLY			
Purchased equipment cost (PEC), $	25,800	103,300	576,300
Equipment installation (40% PEC[a]), $	10,300	41,300	230,500
Piping, electrical, instrumentation (35% PEC[a]), $	9,000	36,200	201,700
Total plant cost (TPC), $	45,100	180,800	1,008,500
Engineering, legal, contingency (37.5% TPC[b])	16,900	67,800	378,200
Total capital investment, $	62,000	248,600	1,386,700
Capital investment, $/dmtpd	31,000	12,400	6,900
(Capital investment, $/dstpd)	(28,100)	(11,200)	(6,300)
CASE II: HOT ACID TREATMENT WITH DEWATERING AND SUPERNATANT TREATMENT			
Purchased equipment cost (PEC),$	113,800	280,300	1,681,300
Equipment installation (40% PEC[a]), $	45,500	112,100	672,500
Piping, electrical, instrumentation (35% PEC[a]), $	39,800	98,100	588,500
Total plant cost (TPC), $	199,100	490,500	2,942,300
Engineering, legal, contingency (37.5% TPC), $	74,700	183,900	1,103,400
Total capital investment, $	273,800	674,400	4,045,700
Capital investment, $/dmtpd	136,900	33,700	20,200
(Capital investment, $/dstpd)	(124,300)	(30,600)	(18,300)

(a) Reference 23

(b) Reference 21

TABLE 39. OPERATING AND MAINTENANCE COSTS FOR HOT ACID TREATMENT ($/DRY METRIC TON SOLIDS)

Plant size, dmtpd	2	20	200
CASE I: HOT ACID TREATMENT ONLY			
Capital cost	7.98	3.20	1.79
Labor	27.39	3.77	0.50
Electricity	1.40	0.91	0.63
Fuel oil	5.18	5.18	5.18
Chemicals, acid	5.00	5.00	5.00
Maintenance materials	2.37	0.91	0.66
Total operating and maintenance cost	49.23	18.97	13.76
CASE II: HOT ACID TREATMENT WITH DEWATERING AND SUPERNATANT TREATMENT			
Capital cost	35.25	8.68	5.21
Labor	30.13	4.11	0.55
Electricity	8.00	2.71	2.1
Fuel oil	5.18	5.18	5.18
Chemicals, acid	5.00	5.00	5.00
lime	2.80	2.80	2.80
Maintenance materials	4.39	1.43	1.04
Total operating and maintenance cost	90.75	29.91	21.88

The total operating and maintainance cost for hot acid treatment is $13.76, $18.97, and $49.23 per dmt solids ($12.50, $17.22, and $44.75 per dst solids) for the 200, 20, and 2 dmtpd plant capacities. Inclusion of sludge dewatering and supernatant treatment increases the costs to $21.88, $29.91 and $90.75/dmt for the respective plant capacities.

To compare the economics of hot acid treatment with other sludge treatment techniques, cost estimates have been developed for: anaerobic digestion, aerobic digestion, lime treatment, and heat treatment. The cost estimates, shown in Tables 40-43, respectively, are based upon capital costs (adjusted to EPA-STPCCI of 288) and recently published operating and maintainance requirements (21). Since many operating costs (such as for energy) have increased at a more rapid rate than the STPCCI, care was taken to adjust all operating and maintainance costs to the same bases used to estimate the costs of hot acid treatment given in Table 39.

The cost estimates of Tables 40-43 are for the treatment or stabilization process only and do not include the cost of sludge dewatering, sludge disposal, or supernatant treatment. However, heat treatment and hot acid treatment both condition sludge for dewatering whereas anaerobic digestion, aerobic digestion and lime treatment are principally stabilization processes that do little to improve dewaterability. To bring the costs to the same basis, the cost of chemicals which must be added to the latter group to prepare the stabilized sludge for dewatering has been included in the cost estimate. The chemical demand of the sludges was based upon generalized estimates given in the literature, and it should be noted that the chemical demand may vary considerably from these estimates depending upon the type of sludge and the wastewater treatment process.

Cost comparisons for various plant capacities are shown in Figure 47. Lime stabilization potentially provides the lowest treatment cost per ton of sludge because of the low capital and operating cost. However, the high chemical cost to prepare the sludge for dewatering makes this process only slightly less expensive than the hot acid treatment process. In addition, sludge disposal costs (not included in this analysis) are increased by the large volume of lime present in the final sludge. In addition, the lime process does not provide metals removal.

The principle economic advantage of hot acid treatment over heat treatment is the much lower capital cost and operation at atmospheric pressure. The advantage of heat treatment is that no chemical addition is required.

Anaerobic digestion is more costly than aerobic digestion because of the higher capital cost resulting from the need for odor control. Aerobic digestion costs are approximately the same as those for hot acid treatment for smaller plant capacities, but the economic advantage of hot acid treatment is greater for larger plants. The main differences are the need for more chemicals to condition the aerobic sludge, and the higher capital costs for aerobic digestion equipment.

TABLE 40. CAPITAL AND OPERATING COSTS FOR ANAEROBIC DIGESTION*

Plant size, dmtpd	2	20	200
Capital cost, $\$ \times 10^5$	0.866	3.82	23.00
Manpower, man-day/year	200	800	4000
Electrical energy, kW-hr$\times 10^{-3}$/yr	80	350	2400
Chemicals[†]			
Lime, kg/metric ton solids	100	100	100
$FeCl_3$, kg/metric ton solids	50	50	50
Capital cost, $/dmt	111	49.18	28.36
Labor, $/dmt	27.4	11.0	5.47
Electrical energy, $/dmt	5.47	2.38	1.64
Chemicals			
Lime, $/dmt	3.00	3.00	3.00
$FeCl_3$, $/dmt	5.00	5.00	5.00
Maintenance materials, $/dmt	7.51	3.87	1.77
Total operating and maintenance cost, $/dmt	159.38	74.43	45.24

[*] Does not include dewatering and supernatant treatment

[†] Reference 24

TABLE 41. CAPITAL AND OPERATING COSTS FOR AEROBIC DIGESTION[*]

Plant size, dmtpd	2	20	200
Capital cost, $\$x10^{-6}$	0.022	1.42	11.0
Manpower requirement, man-days/year	35	140	800
Electrical energy, kW-hrx10^{-3}/year	220	2200	22,000
Chemicals[†]			
Lime, kg/metric ton solids	20	20	20
$FeCl_3$, kg/metric ton solids	100	100	100
Capital cost, \$/dmt	28.32	18.28	14.6
Labor, \$/dmt	4.79	1.92	1.10
Electrical energy, \$/dmt	15.09	15.09	15.09
Chemicals			
Lime, \$/dmt	0.50	0.50	0.50
$FeCl_3$, \$/dmt	9.40	9.40	9.40
Maintenance materials, \$/dmt	2.32	1.68	1.45
Total operating and maintenance cost, \$/dmt	60.42	46.87	42.14

---

[*] Does not include solids separation and supernatant treatment.

[†] Reference 25

TABLE 42. CAPITAL AND OPERATING COSTS FOR LIME TREATMENT

Plant size, dmtpd	2	20	200
Capital cost, $\$ \times 10^{-6}$	.030	.134	.622
Manpower requirement, man-days/year	175	260	400
Electrical energy, kW-hr $\times 10^{-3}$ /year	21	125	750
Chemicals†			
Lime, kg/metric ton solids	200	200	200
$FeCl_3$, kg/metric ton solids	21	21	21
Polymer, kg/metric ton solids	2.5	2.5	2.5
Capital cost, $/dmt	3.86	1.73	0.80
Labor, $/dmt	23.28	3.56	0.55
Electrical energy, $/dmt	1.43	0.86	0.52
Chemicals			
Lime, $/dmt	5.00	5.00	5.00
$FeCl_3$, $/dmt	2.00	2.00	2.00
Polymer, $/dmt	2.50	2.50	2.50
Maintenance materials, $/dmt*	1.88	0.77	0.56
Total operating and maintenance cost, $/dmt	38.95	16.42	11.93

* Does not include solids separation and supernatant treatment.

† Reference 15

TABLE 43. CAPITAL AND OPERATING COSTS FOR HEAT TREATMENT*

Plant size, dmtpd	2	20	200
Capital cost, $\$x10^{-6}$	.079	1.73	15.7
Manpower, man-days/year	200	400	4000
Energy			
Electrical, kW-hrx10^{-3}/yr	60	550	5000
Fuel oil, kwhrx10^{-3}/yr	498	4680	10,880
Capital cost, \$/dmt	102	22.28	20.22
Labor, \$/dmt	27.4	5.48	5.48
Energy			
Electrical, \$/dmt	4.10	3.76	3.43
Fuel oil, \$/dmt	6.13	5.77	1.33
Maintenance materials, \$/dmt	6.92	1.81	1.47
Total operating and maintenance cost, \$/dmt	146.55	39.10	31.93

* Does not include solids separation and supernatant treatment.

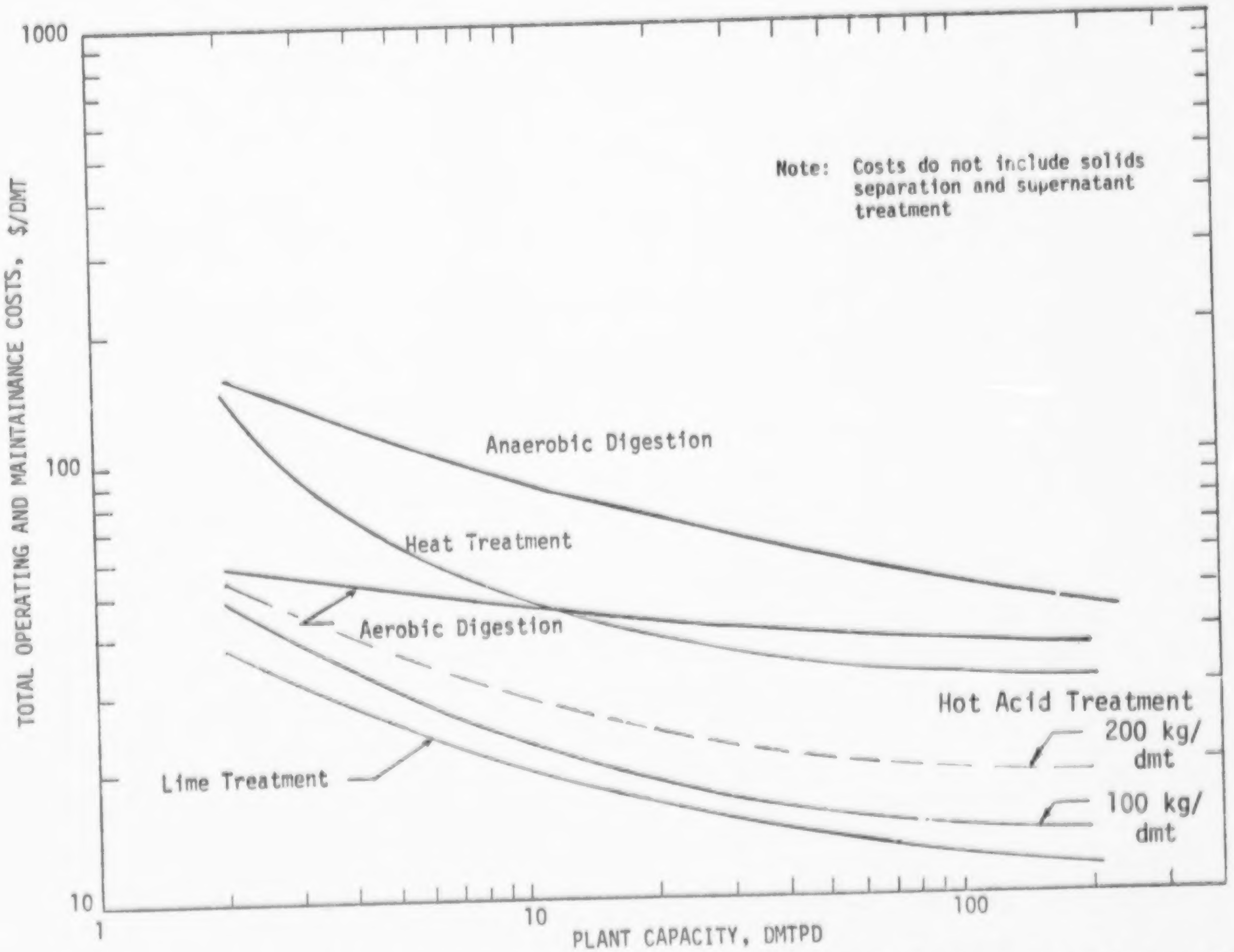

Figure 47. Operating and maintenance cost as a function of plant capacity for various sludge treatment alternatives.

For optimum removal of heavy metals, the costs presented in Table 39 and Figure 47 should be adjusted to reflect an acid usage of 200 kg/dmt rather than 100 kg/dmt. This will add $5/dmt for hot acid treatment only and $7.80/dmt for hot acid treatment with dewatering and supernatant treatment. The dashed curve of Figure 47 shows the cost as a function of plant capacity for hot acid treatment when the process is optimized for heavy metals removal. Total costs, including dewatering and liquor treatment and including capital amortization, for optimized metals removal at plant capacities of 2, 20, and 200 dmtpd would be $98.55/dmt, $37,71/dmt, and $29.68/dmt, respectively.

Based on the above cost comparisons it is concluded that the hot acid treatment process is highly cost competitive with alternative stabilization/conditioning techniques and is particularly attractive where land application of sludge is limited by the concentration of heavy metals in the sludge.

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APPENDIX A

VERIFICATION OF SELECTED ANALYTICAL RESULTS

During the course of the experimental program, questions arose concerning the accuracy of analytical results, particularly those for heavy metals. Therefore a number of samples were submitted to the Municipal Environmental Research Laboratory of EPA (Mr. Vincent B. Salotto) for analytical verification. Samples submitted to EPA were refrigerated prior to shipment and were shipped by air freight.

Analytical results are compared for the various samples in Table A-1. The columns headed by "W" are the results from the Walden Analytical Laboratory; those headed by "E" are the results from the EPA analytical laboratory. In general, there is reasonably good agreement between the results of the two laboratories.

The cadmium results are particularly noteworthy because of the environmental importance of cadmium. One of the specific objectives of this comparison was to verify the high cadmium solubilization (90%) reported by the Walden lab for Brockton WAS (first line of Table A-1). The EPA results do verify the high cadmium solubilization for this test. For the Fitchburg and Milwaukee waste activated sludges the EPA results indicate 50% and 84% solubilization, of cadmium respectively, while the Walden results indicate zero percent for both. For the sample of Brockton WAS injected at various pH's, good agreement was obtained between the Walden and EPA results. It should be noted that, for this latter sample of sludge, the heavy metals proved to be quite difficult to solubilize, and the results should not be considered characteristic of the potential of the hot acid process to solubilize heavy metals.

From a comparison of all the results of Table A-1 it is concluded that the Walden analytical results are at least as consistent as those obtained by EPA. For cadmium, the EPA results suggest that solubilizations could be greater than those reported on the basis of the Walden analytical results.

TABLE A-1. COMPARISON OF METALS SOLUBILIZATION DATA AS DETERMINED BY WALDEN (W) AND EPA (E)

Waste activated sludge	Treatment conditions			Total solids (mg/l)		Zinc						Cadmium						Nickel					
	pH	Temp. °C	Time min			Tot mg/l		Dis mg/l		SOl %		Tot mg/l		Dis mg/l		Scl %		Tot mg/l		Dis mg/l		Sol %	
				W	E	W	E	W	E	W	E	W	E	W	E	W	E	W	E	W	E	W	E
Brockton	2.5	95	10	--	--	32	42	26	32	81	75	1.0	1.1	0.9	1.3	90	123	1.1	1.2	0.7	.24	64	140
	----- Raw -----			25,100	19,620	30	33	<.1	2.0	--	--	1.0	1.0	<.2	.24	--	---	0.6	2.4	<.5	.8	--	---
Fitchburg	2.5	95	10	--	--	29	40	17	25	58	59	.34	.36	<.2	.28	0	50	26	30	16	15	60	49
	----- Raw -----			40,600	68,580	30	60	.1	3.2	--	--	.34	.40	<.2	.20	--	---	23	47	.7	.8	--	--
Milwaukee	2.5	95	10	26,700	25,530	76	63	30	30	39	41	5.9	5.2	<.2	4.4	0	84	5.7	7.2	4.3	4.0	75	55
	----- Raw -----					59	54	<.1	5.8	--	--	4.7	4.4	<.2	.2	--	--	3.7	4.4	<.5	.12	--	--
Brockton	1.0	95	10			69	62	54	59	78	95	4.0	4.0	2.5	2.7	62	66		3.2		2.0		55
	1.2	95	10			74	68	60	54	81	79	4.3	4.0	2.1	1.9	49	46		2.8		2.0		65
	1.5	95	10			74	66	49	45	66	68	4.4	4.0	0.3	.28	7	4		2.8		1.2		30
	2.0	95	10			69	62	14	22	20	34	4.0	4.0	<.2	.24	0	3		1.2		.28		-35
	2.5	95	10			68	65	2.7	5.6	4	7	4.0	4.0	<.2	.20	0	2		1.2		0		-76
	----- Raw -----			49,000	48,160	--	59	0.2	1.2	--	--	--	3.7	<.2	.12	--	--		.80		.52		--

TABLE A-1. CONTINUED

Waste activated sludge	Treatment conditions			Total solids (mg/1)		Chromium						Lead						Copper					
	pH	Temp. °C	Time min			Tot mg/1		Dis mg/1		Sol %		Tot mg/1		Dis mg/1		Sol %		Tot mg/1		Dis mg/1		Sol mg/1	
				W	E	W	E	W	E	W	E	W	E	W	E	W	E	W	E	W	E	W	E
Brockton	2.5	95	10	--	--	240	196	18	15	8	7	12	6	1.3	.80	11	13	15	16	<.5	.8	0	4
	-----	Raw	-------	25,100	19,620	240	180	<.5	.8	--	--	11	9.6	<1	.0	--	--	15	16	<.5	.12	--	--
Fitchburg	2.5	95	10	--	--	110	130	.6	1.6	0	1	130	27	<1	0	0	0	66	73	<.5	.4	0	0
	-----	Raw	-------	40,600	68,580	120	233	<.5	.8	--	--	140	129	<1	0	--	--	69	125	<.5	.8	--	--
Milwaukee	2.5	95	10	26,700	25,530	147	121	1.9	3.2	1	1	—	13	--	.8	--	6	14	14	<.5	.4	0	1
	-----	Raw	-------			124	98	<.5	2.4	--	--	—	3.8	--	0	--	--	11	12	<.5	.2	--	--
Brockton	1.0	95	10				424		324		76		3.2		12		375		47		1.6		3
	1.2	95	10				404		284		70		2.8		11		393		40		.4		1
	1.5	95	10				408		148		36		4.2		3.2		76		35		.8		2
	2.0	95	10				432		24		5		3.6		0.4		11		36		.4		1
	2.5	95	10				408		10		2		6.4		0		0		37		.4		1
	-----	Raw	-------	49,000	48,160		374		3.2		--		7.6		0		--		33		.12		--

APPENDIX B

LABORATORY REPORT ON CENTRIFUGATION TESTS

BIRD MACHINE COMPANY, INC.
SOUTH WALPOLE, MASSACHUSETTS

LABORATORY REPORT NO. 8876

Customer:	Abcor, Inc. Wilmington, MA
Material:	Brockton Waste Activated Sludge #599240
Problem:	Clarification
Test:	Preliminary
Test date:	July 20, 1977
Witnesses:	Dr. Kenneth McNulty Ms. Ann Malarkey

Sample No. 129 (Rec'd 7/20/77)

Six (6) liters of a waste activated sludge were received in the laboratory for preliminary centrifugal testing.

The sludge was obtained by the witnesses from the Brockton, MA STP and pretreated before arriving at the laboratory. The sludge was identified only as WAS. A more exact definition of the sludge would be helpful; i.e., where the sample was collected, time of sampling.

The sludge received was still hot. The sample contained 3.59% total solids by weight, 2.16% dissolved solids in the mother liquor.

Problem

A new sludge treatment process has been developed by Dr. Fremont of Champion International. Further studies to more fully refine and design a treatment system are being carried out by Abcor, Inc.

This new process is an acid/heat treatment for raw sludge. Acid is added to the sludge to lower the pH to 2-3 and the sludge is heated to 90-100°C. Many of the heavy metal compounds dissolve providing a solids product which has better soil conditioning characteristics. Improved settling, filtration, and centrifugation have been noted in laboratory tests with treated sludge.

Vacuum filtration has been ruled out as a means of dewatering since the sludge is to be processed hot and cooling would be needed prior to filtration.

The objective of this test is to demonstrate the ability of a centrifuge to dewater this new-type waste activated sludge.

A large scale test will be run once the sludge characteristics are defined.

Test

Spin tests were run on the sludge as received at 90-100°C. The new test tube spinner was used to allow for variations in centrifugal force. The data is included on pages 1-1 and 1-2. (Note: Much of the data was given in cryptic notation and has not been included in this appendix).

Increased centrifugal force shows a direct effect in settling out suspended solids and producing a firmer cake. The settled solids do not have much body (bulk) since a glass rod readily penetrates into 50% of the cake.

Flocculants including alum, ferric chloride and lime were used to agglomerate the solids to aid in clarification. All of the polymers tested on the as received sludge showed only minimal, if any, agglomeration. The polymers used included Allied Colloids, Hercules, and American Cyanamid. Polymers used in conjunction with others of opposing charge showed no improvement in agglomeration. A combination of lime and polymer seemed to work best in providing clarity and firm cake. These spin tests are also included on pages 1-1 and 1-2. (Not included herein).

Both lime and polymer used together would produce the best results as noted in the spin tests.

The batch pulp centrifuge was also run at varying gravitational forces on as received sludge and flocced slurry.

Cake solids are low and recovery poor without pretreatment. The best results are obtained where lime and polymer are used together. This data is attached on pages 2-1 and 2-2. (Not included herein).

Conclusions

1. This waste sludge or one similar to that tested would be a good application for a Bird Continuous Solid Bowl Centrifuge.

2. Since the cake product will be sold as soil conditioner and will probably need to be neutralized to reduce residual acid content, lime should be added.

This will both add bulk to the cake, to produce a more easily centrifuged material, and neutralize the acid content of the final product. The final cake material would also have improved soil conditioning properties. The lime dosage will have to be defined more exactly in large scale tests but would be in the range of 500-1000 lbs lime/ton dry solids of sludge.

3. Polyelectrolytes would be required for optimum clarification. The preliminary test indicated about 1 lb/ton dosage for +90% solids recovery.

4. The expected cake product would be directly related to the amount of lime addition. The more lime, the drier the cake product that would result.

5. A large scale test would be recommended. The amount of lime to be allowed should be determined prior to testing.

MMangion:nt/22

NOTE:

Allied Colloids Percol 763

Cost = $1.50/lb in bulk
$2.50/50 lb bag for one bag only

1 lb/ton dosage = $2.50/ton max. cost

Lime

Cost = 2¢/lb

500 lb/ton dosage = $10/ton cost

BIRD MACHINE COMPANY, INC.
SOUTH WALPOLE, MASSACHUSETTS

Addendum to: Laboratory Report No. 8876

Customer: Abcor, Inc.
850 Main Street
Wilmington, MA

Material: Brockton Waste Activated Sludge

Problem: Clarify and Dewater

Test: 6" Bird Continuous Solid Bowl Centrifuge

Test date: April 20, 1978

Witness: Mr. John Harland - Engineer for Abcor

Sample No. 127 (Rec'd April 20, 1978)

Two 55-gallon drums containing Brockton waste activated sludge were delivered to the laboratory for large scale testing purposes.

Sample as received contained approximately 2.92% total solids by weight and had a specific gravity of 1.01 @ room temperature. Slurry was prepared for testing by heating to 95° then acidifying with sulfuric acid to a pH of 1.94.

Problem

Abcor is studying a new process for waste treatment described as the "Hot Acid Process", the principle objective being to dissolve and remove heavy metal compounds making a solids product which has better soil conditioning characteristics.

Pilot plant operation will require a deliquoring device which will handle 5 to 10 gallons per minute.

As dry a cake as possible is desired, and lime or flocculants cannot be used as they might precipitate the solubilized metals.

Tests

Five test runs were completed, for data obtained. Please note data sheet appended to this report.

Variables investigated were machine speeds of 6000 and 3500 RPM, equivalent to 3000 x G and 1000 x G, respectively.

Intermediate pool volume used during Run #1 was increased to the maximum for Runs #2 through #4 and Run #4 was made with increased cake retention time in an effort to produce a drier cake.

Discussion

Test results show that acidified Brockton waste activated sludge would be a possible application for a Bird Continuous Solid Bowl Centrifuge. However, the restriction on the use of flocculants limits ability to obtain good recovery of feed solids as cake product.

Samples of feed, cake and effluent from each run were taken by the witness for analysis.

TABLE B-1. SOLID BOWL CENTRIFUGAL TEST DATA FOR BROCKTON WAS AT pH 1.94

SOLID BOWL CENTRIFUGAL TEST DATA

Customer: Abcor - Wilmington, MA

Material: W.A.S.

Date: 4/20/78

Run no.	1	2	3	4
Feed: % solids	3.64	3.64	3.64	3.64
Sp. gr.	1.0	1.0	1.0	1.0
GPM	0.73	0.70	0.695	0.559
PPH solids in feed	13.29	12.75	12.65	10.18
Temp., °C	95	95	95	95
Cake: % solids	36.25	17.89	25.81	26.88
PPH wet	2.0	15.0	9.33	9.33
PPH dry	0.72	2.68	2.4	2.5
Effluent: % solids	2.84	2.85	2.47	3.09
Percent recovery	23.84	25.81	35.54	17.07
Machine RPM	3500		6000	
Force x gravity	1000		3000	

ADDENDUM

EVALUATION OF HOT ACID TREATMENT FOR HOT ACID TREATMENT FOR MUNICIPAL SLUDGE CONDITIONING

(EPA-600/2-80-096)

After completion of this report, the U.S. Environmental Protection Agency (EPA) had an engineering assessment made of the Walden hot-acid process for removal of heavy metals from municipal sludge. The results of this assessment will eventually be available as an EPA report. In the interim, an abstract of the report can be obtained from:

R. V. Villiers, Project Officer
Municipal Environmental Research Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268